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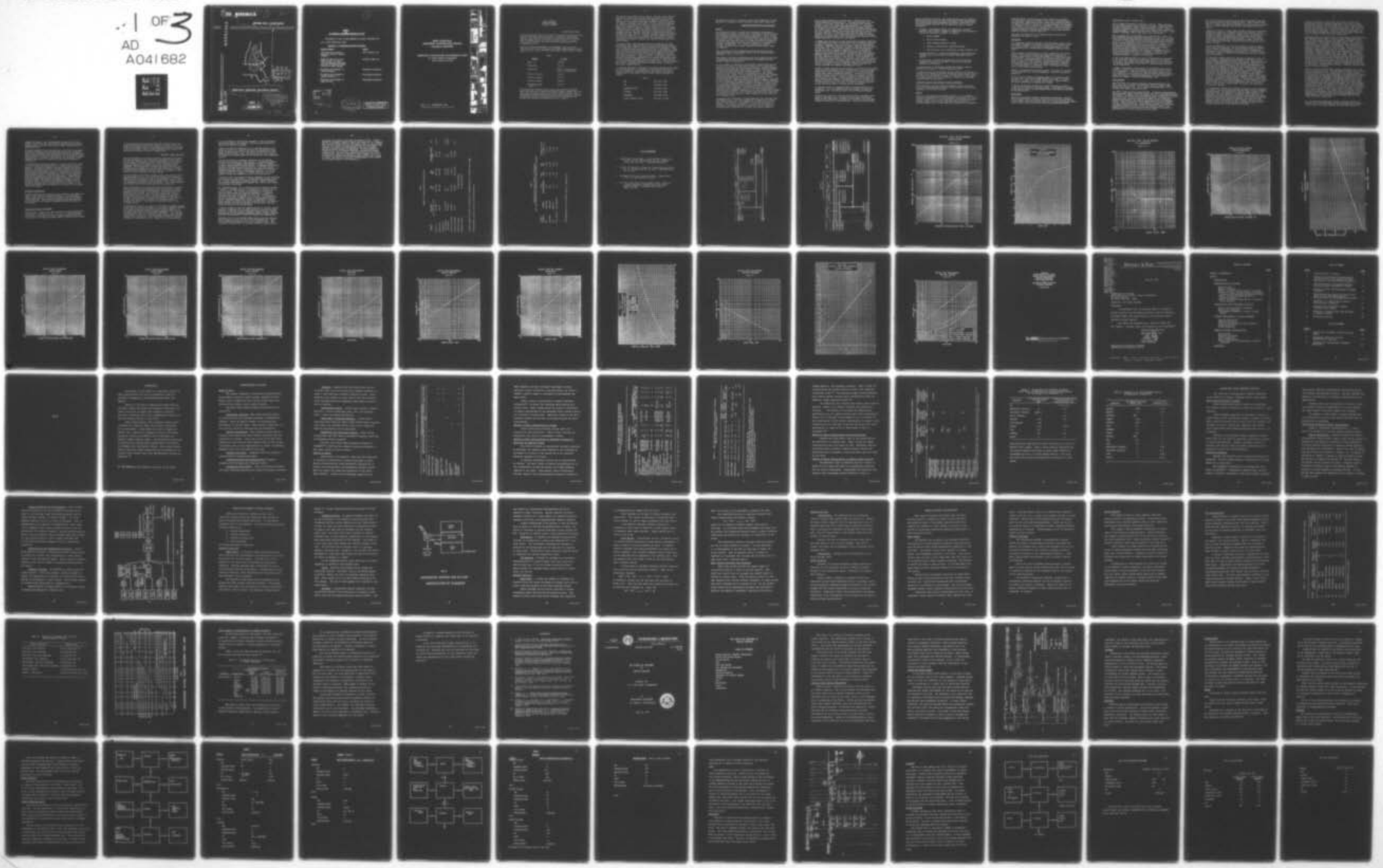

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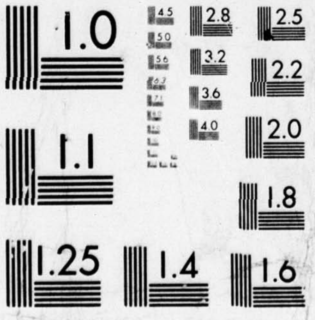

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THE MERRIMACK:

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DESIGNS FOR A CLEAN RIVER

CONSULTANT'S INDUSTRIAL WASTEWATER PROFILES

ANNEX C

⑪ AUGUST 1971

⑫ 194p.

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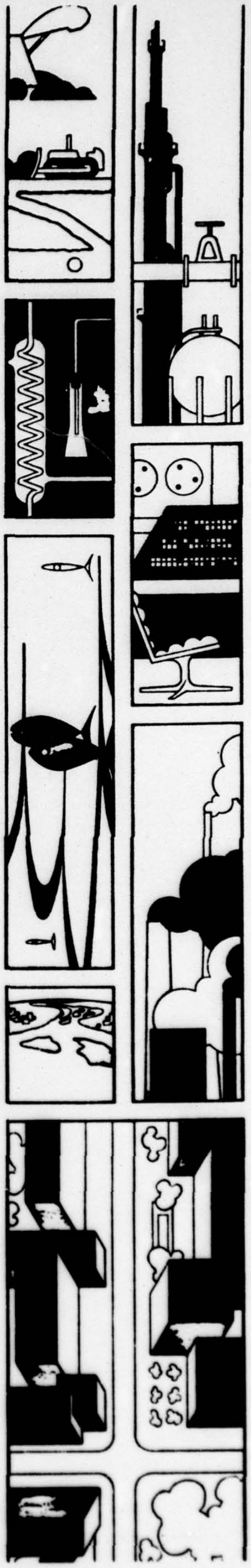
ANNEX C
to
THE MERRIMACK WASTEWATER FEASIBILITY STUDY

Following is a list of data prepared by private consultants for use in this feasibility study:

Annex No. C - Industrial Wastewater Profiles

Title of Report	Author
Brief Overview, Industrial Wastewater Profile, Plastics Industry,	Roy F. Weston, Inc.
Report to Dept of the Army, North Atlantic Division, Corps of Engineers, New York, New York on Industrial Wastes Profiles of Metal Plating,	Metcalf & Eddy, Inc.
The Nature and Treatment of Textile Effluent,	Thorstensen Laboratory
The Nature and Treatment of Tannery Effluent, and	Thorstensen Laboratory
The Nature and Treatment of Paper Effluent.	Thorstensen Laboratory



BRIEF OVERVIEW
INDUSTRIAL WASTEWATER PROFILE
PLASTICS INDUSTRY

MERRIMACK WASTEWATER MANAGEMENT STUDY
U.S. ARMY CORPS OF ENGINEERS
NEW ENGLAND DIVISION

ROY F. WESTON, INC.
ENVIRONMENTAL SCIENTISTS AND ENGINEERS

BRIEF OVERVIEW
INDUSTRIAL PROFILE
PLASTICS INDUSTRY

OBJECTIVE AND SCOPE

This brief overview report will present an assessment of some significant industrial wastewater disposal aspects of a portion of the plastics industry, with particular reference to a feasibility study of a wastewater management program for the Merrimack River Basin. Time and effort were limited and, therefore, the scope of the report will be correspondingly brief.

Based on information developed in the management study to date and furnished by the Corps of Engineers, the products manufactured by plastic industry plants in the study area include those listed in Table 1 following.

TABLE 1

PRODUCT	SIC CODE
Nylon - 6	28219-40
Polystyrene	28213-10
Polyethylene	28214-11 (High Density) 28214-12 (Low Density)
Polyvinyl Chloride	28212-10
Polyvinyl Acetate	28212-20
Polyvinyl Alcohol	28212-30
Butadiene-Styrene Resins	28213-20

The manufacturers producing these products whose plants are located within the study area include Borden Chemical Company, Foster-Grant, Inc., Great American Plastics Company, and Paragon Plastics Company. The investigations conducted and the discussions presented here with reference to wastewater quantities and characteristics will be focused on the products and processes represented by the list in Table 1.

The plastics and synthetic resins industry, like the organic chemical industry as a whole, cannot be described meaningfully as a single entity. There is a very wide variety of products represented, manufactured by a multitude of processes, although in some cases the bulk of a particular product may be made by a single processing technique. For example, approximately 85 percent of the polyvinyl chloride is made by the suspension process. However, there are still significant differences, not only among the various manufacturers but also between different plants of the same manufacturer, due to varying in-plant wastewater control practices, variations in degree of utilization of manufacturing plant capacity, differing suspending agents and catalysts or initiators used, etc. For instance, for three separate polyvinyl chloride resin plants using essentially the same process, a 15-fold difference in the amount of BOD per unit product has been observed in plant effluent.

On the other hand, sufficient data were not available nor was time available to obtain data specific to the plants andprocesses involved in the study area to permit a specific evaluation of wastewater generation and disposal practices pointed exclusively at those plants. Therefore, readily available published data and some unpublished information have been used to characterize generally the wastewater loading and quality and to serve as a basis for comment on production, treatment and disposal practices. A better basis for an evaluation such as this should be available upon completion of the current EPA-sponsored study to define effluent guidelines for various industries. These studies are directed toward the development of a definition of raw waste loadings, base level of treatment and the best available degree of treatment at the current state-of-the-art.

An objective specified in information furnished by the Corps of Engineers as an "ultimate goal" is the removal of "all possible pollutants". A further definition of that objective has been given as the "maximum feasible purity" with regard to certain water quality parameters as follows:

TABLE 2

BOD	less than 2 mg/L
COD	less than 5 mg/L
Suspended Solids	less than 2 mg/L
Nitrogen	less than 1 mg/L
Phosphorus	less than 1 mg/L
Total Dissolved Solids	less than 100 mg/L

The general discussion of treatment alternatives included here is based generally on a program to attain the above listed quality objectives.

MANUFACTURING PROCESSES AND WASTEWATERS

General

The following discussion of manufacturing processes and wastewater characteristics, sources, loadings, etc. associated with those processes will be restricted essentially to polymer production. That is, wastewater problems associated with monomer manufacture will not be included. The polymers listed in Table 1 as including those manufactured by plants in the Merrimack study area does not include all polymers manufactured, although a large proportion of the total production is represented by the types included here. For instance, polyethylene, polyvinyl chloride, and polystyrene polymers represent the three largest types in production.

Some information has been developed in the past characterizing the wastewater problem of the plastics industry and the related (monomer) industries. (1), (2), (3), (4).

These reports plus some unpublished data and file information were used to develop the preliminary characterization of wastewater from the plastics industry presented here.

As with a number of industries, the variations in cooling water use and recirculation practice in the plastics industry exert a significant influence on total water use and on effluent quality. Generally speaking, cooling water from plastics manufacturing is "clean" in the sense that it does not directly contact the processed materials. Of course, where very high effluent quality is the objective, as with "maximum feasible purity", (Table 2) in the ultimate goal of this study, blowdown from recirculated cooling systems could not be considered "clean". Corrosion and scale prevention additives are commonly used, as are slime control chemicals. These might include nitrogen or phosphorus compounds, as well as some metallic compounds, notably chromium. The use of mercury, zinc, and other organo-metallic compounds for biological growth control in recirculating cooling systems is being supplanted by the use of more degradable organic compounds. The objective of low dissolved solids (less than 100 milligrams per liter) in an effluent is essentially impossible without treatment (deionization) for recirculated cooling systems using evaporative cooling, since raw water dissolved solids content will be increased in such systems by a factor between two and ten times the initial concentration.

The potential for elimination of process materials with relatively high pollutional impact or for their substitution by materials of lower or zero pollution potential is considered to be relatively low for this industry. The principal raw material is, of course, the monomer(s) required for the specific polymer (or copolymer) being manufactured. No substitution is practical for the basic raw material, except by total product elimination or substitution by a product with lower pollution-generation characteristics. The overall potential for such practice is not great, since needs, uses and markets for different polymers, plastics and resins have been generated, to a large extent, by the peculiar and specific properties of the individual products. An in-depth study of the industry to determine and evaluate interchangeability of various products, particularly substitution of low-pollution-per-pound materials, is required to assess the real impact of this approach. Of course, such a study would need to consider the optimum waste control and pollution impact from raw material production through monomer manufacture to product use and disposal.

A somewhat more potentially fruitful application of material elimination or substitution as a means of pollution control is related to additive and control compounds, such as initiators or catalysts, delusterants, inhibitors, suspending and dispersing agents, light and heat stabilizers, antioxidants, etc. The different, specific and desired properties of the many varieties of polymeric compounds are, to a large degree, a function of types and amounts of these materials used. Along with actual thruput capacity of equipment, the specific modifying compounds and their amounts or combinations are the most jealously guarded and best kept competitive secrets in the industry. A real assessment of the potential of this approach on a broad base would require an industry-wide cooperative study. Of course, there is a significant economic incentive to individual plants and companies faced with stringent effluent quality requirements to balance (optimize) material selection with effluent treatment and disposal requirements and costs.

Probably the most promising in-plant approach to controlling environmental impact of plastics manufacturing is in the recovery, recycle and reuse of materials in the polymerization operations. To a very significant degree, these steps are practiced currently. The efficiency of such measures has been dictated in the past largely by "recovery economics" related to material costs. Effluent treatment and disposal costs and their impact on the selection of the degree of recovery efficiency of monomers, oligomers, solvents, and other materials have not been nearly as significant a factor in the past as they would represent with the current and future trends in effluent quality requirements.

In some cases, waste or recovered product may be depolymerized for reprocessing. This is not generally the case, however, and would not be expected to be a significant factor in controlling environmental impact.

Practically all plastics and polymer plants practice wastewater segregation to some degree now. Non-contact cooling waters are usually separate within the process, although quite frequently these and other streams are combined in a common effluent. For the very high effluent quality requirement defined by the "maximum feasible purity" objective mentioned previously, the most useful segregation scheme would probably be to classify and combine wastewaters in relation to the type of conditioning/treatment necessary for the appropriate reuse or disposal alternative:

A. Inorganic - contaminated streams, with essentially no organic pollutants where chemical treatment or membrane or resin processing would be an appropriate treatment, for example:

    1. Boiler blowdown

    2. Cooling system blowdown

    3. Water treatment backwash or sludge

    4. Softener or demineralizer regeneration wastes

    5. Process wastes, such as washwaters, scrubber effluents, etc.

B. Concentrated organic - contaminated wastewaters, where specialized treatment such as incineration or recovery techniques could be applied.

C. Dilute organic - contaminated wastewaters, where conventional secondary (biological) or secondary - tertiary (e.g. physical-chemical) can be applied.

A brief discussion of applicable treatment and disposal systems is presented in the section "treatment Systems and Costs".

It should be noted that the effluent quality implied in the "maximum feasible purity" objective should be equivalent to water quality required to permit a very high degree of reuse. The feasibility of such reuse in a specific plant can only be defined as a result of an individual study and design for that case.

Information Sources for Individual Polymers and Resins

Brief discussions and data relative to specific polymers and resins, as well as references where additional information may be obtained are presented in the following sections.

Nylon 6

Nylon 6 is a polyamide-type condensation polymer. It is formed by continuous polymerization of a single monomer, caproloctam, in a tubular reactor at about 250°C. A chain terminator, such as acetic acid, may be used. Water or the Nylon 6,6 salt serves as an initiator. A titanium dioxide slurry is often added as a delusterant in the reactor.

Unreacted monomer and low molecular weight oligomers are stripped from the reactor product for recovery. The resin is extruded, cooled and pelletized. Other additives may include light and heat stabilizers. The degree and method of extraction of unreacted monomers and oligomers is a function in part of the use for the polymer, since these materials afford plasticizing properties. Although data are lacking, the basic processing techniques involved would indicate a lower water pollution potential for Nylon 6 than for Nylon 6,6.

Some data from reference (1) for composited Nylon 6 and Nylon 6,6 wastewaters are given in Table 3.

Polystyrene

The fundamental processing technique in styrene polymerization is batch. The monomer frequently is purified by distillation or by caustic wash. This step may be done at the point of monomer manufacture or at the polymerization plant - which affects the wastewater loading at either point.

Three processes are used alone or in certain combinations for polymerization: bulk or mass polymerization; suspension polymerization; emulsion polymerization for latex manufacture; or a combination of bulk and suspension. Bulk polymerization is reported to be the most common. There is very little water contact in the pre-polymerization or bulk stage or process. In the suspension and emulsion process, suspending and dispersing agents are used in an aqueous suspension or emulsion. An oil-soluble catalyst is frequently used in the suspension process, usually of the organic peroxide type.

Monomer is stripped from the reactor product. The polymer is separated by centrifugation and is further processed by filtration, washing and dewatering.

Principal routine sources of wastewater appear to be suspension water and wash water. Water use has been reported to be about 1.5 gallons per pound of product, not including cooling water. Reuse of water in polystyrene manufacture is reported as not common.

A material substitution possibility to reduce environmental impact is in the use of initiators or suspending agents. These materials influence product quality greatly and such effects must be considered and evaluated in such substitution.

Polyethylene

There are a multitude of grades of polyethylene manufactured. Manufacturing (polymerization) techniques are tailored to the properties desired in the product. The most important types are low density polyethylene (LDPE). usually branched chain polymers; and high density polyethylene (HDPE), predominantly linear in polymer form.

LDPE is formed at pressures in excess of 10,000 psi. Small quantities of free radical sources, such as oxides of nitrogen or organic peroxides are used as catalysts in either stirred autoclave or tubular reactors. Solvents are generally not used, except for benzene or water occasionally. Unreacted monomer is flashed from the reactor product for recycle. Molten polymer is extruded, usually under water, and is pelletized.

HDPE is polymerized at considerably lower pressures than is LDPE. For the high density product, metal-based catalysts are used, e.g., aluminum alkyls and titanium tetrachloride in the Ziegler process, chromium oxide on silica or silica-alumina in the Phillips Petroleum process. Reaction may be in a solution-form process or in a particle-form process. In the former, ethylene dissolved in a hydrocarbon solvent is contacted with the catalyst; following completion of the reaction, the catalyst is separated and excess monomer and solvent are flashed off. In the particle form process, ethylene and catalyst are suspended in a circulating non-solvent hydrocarbon, (e.g. pentane) in a tubular reactor. Polymer precipitates as it forms, is settled and removed and the hydrocarbon-monomer is flashed off and recycled.

In both cases (HDPE and LDPE), the level of contamination of wastewater is low, principally because of minimal water contact in the process. At the end of the process, where the product may be chilled and chopped into pellets, recirculated chilled water is frequently used, with very little contamination.

A summary of wastewater characteristics from polyethylene manufacture is given in Table 3, based on information from several sources, principally reference (1). The reason for the wide spread of water use per unit production is not clear at this time, but may be related to cooling water use practices. Ethylene polymerization is a highly exothermic reaction and imposes a significant cooling water load.

Vinyl Polymers

There are three vinyl polymers reported as being manufactured in the Basin study area - polyvinyl chloride (PVC), polyvinyl acetate (PVAC) and polyvinyl alcohol (PVA). On an industry-wide volume basis, by far the most significant of the three is PVC.

Most PVAC is made by emulsion polymerization. An emulsion recipe generally contains monomer; water; protective colloids (e.g. PVA, hydroxyethylcellulose, many others); surfactants (e.g. most commonly anionic sulfates and sulfonates, but cationic and non-ionic emulsifiers are possible); initiators (e.g. organic peroxides and other free-radical types); buffers (phosphates, acetates, bicarbonates) and molecular weight regulators (e.g. aldehydes, thiols). Types and amounts of recipe additives are controlled largely by product properties desired. Polymerization proceeds to a sufficiently high degree of conversion (99 percent) that monomer stripping is not commonly justified or practiced on the basis of monomer use economics. Copolymers with a variety of materials are also made.

Very little information and data are available on wastewater quantities and characteristics from PVAC production alone. Table 3 presents some data for a single source which can probably be considered fairly "typical". PVAC is a frequent copolymer with PVC and is discussed later in that context.

Commercially, polyvinyl alcohol (PVA) is made by hydrolysis (alcoholysis) of polyvinyl acetate, in a methanol solution with methanolic sodium methoxide or other alkaline agents. Acetic acid is a by-product of the polymer gel formed. Wastewater results from product neutralization, recovery and drying and from methanol recovery. Data on wastewater quantities and characteristics and information on water use and reuse and on reactant and by-product recovery practices and potential are not readily available.

Polyvinyl chloride (PVC) is one of the three major plastics, between polyethylene and polystyrene. PVC can be made by suspension, emulsion, bulk or solution polymerization. Bulk and solution polymerization processes are not yet commercially very significant, although the bulk (two-stage) process has recently been developing and may have increased future significance.

The suspension process accounts for the bulk of production in the vinyl resin industry, representing about 85 percent of the total, with the emulsion process accounting for most of the balance. Both polymerization methods are batch operations and use certain organic suspending, dispersing or emulsifying agents (e.g. PVA, gelatin, methylcellulose for the suspension process or detergents for the emulsion process) to homogenize the vinyl monomers in the water phase. Polymerization reactions are initiated by the addition of catalysts (e.g. organic peroxides) under controlled temperature and pressure conditions. Upon completion of reaction, the unreacted monomer(s) is stripped from the reacted batch and is recovered. When using the suspension process, the reacted content is a coarse particulate polymer suspension which is centrifuged to dewater and separate the PVC product. In the emulsion polymerization technique, PVC in the reacted batch appears as latex (submicron colloidal particle emulsion) at PVC solids concentration of 30 to 40 percent by weight. Spray drying is used to obtain PVC polymer from latex when a dry product is desired.

In the suspension polymerization process, the majority of the wastewater flow results from the centrifugation operation where polymer is dewatered and water-washed. The cleaning and rinsing of reactor vessels is the other major source of wastewater. In addition, small quantities of wastewaters with high levels of contamination result from spills during product batch transfers and reactor sampling, from cleaning contaminated floors and from periodic dumps of wastewaters upon emptying of the knockout vessel at the monomer stripper. However, the only continuous wastewater stream from the suspension polymerization process is the centrate from the centrifugal separation of product.

Wastewater generation in the emulsion plant normally results from cleaning and rinsing of production equipment, from losses of polymer emulsion when cleaning, and from product spills during batch transfers and reactor samplings which are washed into the sewer. The cleaning of tank car loading areas, which are contaminated with product spills, is another source of wastewater. There is no continuous wastewater flow from the emulsion polymerization PVC process and frequent intermittent flow is a result of floor and trench cleaning water.

Wastewaters from vinyl polymerization processes contain suspended material, both settleable and colloidal in nature, soluble carbonaceous matter and, to a minor degree, foam and odor producing substances. The suspended solids in the wastewater are polymer solids. A majority of suspended solids in the suspension polymerization process wastewater are coarse and readily settleable. This wastewater, after brief settling, generally contains turbidity less than 200 mg/L. The emulsion process wastewater suspended solids are mostly colloidal in nature and are non-settleable. BOD-exerting materials in the wastewater are composed of dispersants, suspending agents, emulsifiers, stabilizers, inhibitors and reaction initiator chemicals lost to the sewer. Other significant sources of organic matter in the wastewater are the unreacted and unrecovered vinyl monomers and certain formula additives such as acrylates and acrylonitrile used in PVC latex. Generally, the reaction vessels in the suspension polymerization process are cleaned and scoured with solvents prior to the final water rinsing and preparation of the vessel for the new mix. Although solvent recovery is generally employed, some solvent is lost to the sewer.

Using the suspension polymerization process, both homopolymer and copolymer may be manufactured. The most common copolymer is that resulting from the condensation of vinyl chloride and vinyl acetate monomers. While there are no significant differences in the manufacturing processes for making homo- and co-polymers, the resultant wastewaters are quite different because of difference in the degree of monomer loss to the wastewaters and in the nature of the suspending agents used. Based on the examination of volatility and water solubility characteristics of the monomers, different quantities of monomer loss to the wastewater could be anticipated. For example, vinyl chloride is a gas at ambient temperature and is sparingly soluble in water, while vinyl acetate boils at 73°C and is soluble in water up to 2 percent by weight. A significantly higher quantity of vinyl acetate than vinyl chloride could be expected in the wastewater, even after monomers recovery by stripping. Concentrations of vinyl chloride and vinyl acetate detected in two random samples of centrate from the centrifugation operation were 3 mg/L and 300 mg/L respectively.

For the suspension polymerization process, copolymer manufacturing generates much higher waste BOD_5 than does the homopolymer production. A major cause for high BOD wastewater from copolymer production is probably the loss of vinyl acetate monomer to waste due to lesser volatility and higher water solubility as compared to vinyl chloride monomer, which is the only basic chemical used in polymerization to make homo-polymer.

Different wastewater flows and waste loads result from the suspension and emulsion processes and from production of homo- and co-polymers. Based on data collected from three separate PVC plants, average wastewater quantities and qualities generated per million pounds of product manufactured for a "normally" operated plant are presented in Table 4, comparing those results to summarized survey data as published in reference (2).

The variability illustrated on Table 4 is illustrative of the problem in trying to generalize information for a complex industry such as plastics. The specific processes and types of products must be considered in the characterization of wastewater quality and loadings. The unique and secret aspect of vinyl resin manufacture is the suspending agent and method of suspension. Information on the specific type and concentration of suspending agent used is often sketchy or unavailable to anyone other than the manufacturer. Generalizations about the oxygen demand potential or other characteristics of PVC wastewater without the background knowledge of causative materials can be misleading. The range of data presented in Table 3 for PVC wastewater characteristics is based primarily on reference (2) and illustrates order-of-magnitude values, as is the case for all products shown on that table.

Butadiene-Styrene Resins

Butadiene copolymers of styrene are mainly prepared in the composition range to yield synthetic elastomers (rubbers). Styrene-butadiene rubbers (SBR) account for a very large proportion of total synthetic rubber production. Generalized data relating wastewater quantities and characteristics to production parameters were not derivable for this profile.

Relation of Plants in Study Area

The data shown in Table 3 have been transcribed or derived from information given in reference (1), (2), (3), (4). In those references, most of the loading data were given in weight of pollutant per unit of production. To compare the general effluent quality level of plants in the study area to the more generalized data, loadings were translated into equivalent concentration ranges as reported in Table 3. A comparison of effluent quality for Merrimack Basin plants, as recorded so far in the study, to Table 3 shows that these plants effluent concentrations are within the range or somewhat below.

TREATMENT SYSTEMS AND COSTS

Selection and design of treatment systems for wastewaters from plastic and resin manufacturing are a function of wastewater characteristics and loadings, effluent quality objectives and specific local factors, such as climate, available space, etc. Some information relating wastewater character and loadings to specific products has been presented. This information is sketchy; additional studies to expand the data base are needed and are in fact being conducted or planned by EPA and others (Effluent Guidelines studies as an example). Useful results will not be available for some time yet.

For the purposes of this basin management study, some effluent quality objectives have been set, particularly the "ultimate goal of maximum feasible purity" as defined in part by the parameters listed in Table 2. Some lower quality objectives would be appropriate for interim goals or for wastewaters discharged to municipal sewers. These interim effluent quality goals need to be defined specifically for each case.

Specific pollutants to be removed and their concentrations or loadings should be determined from wastewater sampling and analysis programs designed for the individual case objective. Projections to a future design base must be made. Sets of effluent quality objectives for different time or quality goals need to be established. Based on those factors, then, the units of treatment/disposal system can be selected to match the duty and "ball-park" estimates of the costs can be made, using guidelines, procedures and estimating factors in References (3) and (4). The approach is described further in the following sections.

In Reference (4), Figure 4 on page 28 is a Wastewater Treatment Sequence/Process Substitution Diagram prepared for the organic chemicals industry. This diagram is generally applicable to the plastics industry also. This generalized diagram shows two general treatment trains, one for "dilute" and the other for "concentrated" wastewaters. This breakdown is appropriate in the case of plastics plants as well, where such segregation may be appropriate. The diagram does not show all possible treatment unit processes of course. However, most of those prevalent in use or frequently considered for wastewater of the type common to the plastics industry are included. Each unit process alternative shown on the diagram is numbered.

Figure 13 on page 77 of Reference (3) is a modified version of the processes substitution diagram illustrating for petrochemical wastewaters the general level of effluent quality attainable from various stages of the treatment system. The general quality levels shown on the diagram can be applied generally to plastics and resins wastewaters as well.

From the information on wastewater characteristics and loadings, effluent quality objectives (final effluent or intermediate effluent or reuse), and the treatment effectiveness of stages, a treatment system or process sequence can be selected. For example, the principal treatment requirements encountered with vinyl resin (PVC) process wastewaters are the removal of settleable and colloidal solids and of soluble biodegradable organic (carbonaceous) material. An on-site treatment system for attainment of "maximum feasible purity" would probably include units numbered 1,2,4,5,7,9,13,15,16,17,19,23.

Alternative trains are possible of course, depending on local conditions, in plant control, reuse potential, alternative sludge disposal points, etc. Perhaps, depending on wastewater strength, specific additives and modifiers used, manufacturing schedule, etc., units 9 and 13 might be eliminated in some cases.

For intermediate goals, such as "the equivalent of secondary treatment of sewage", a treatment train for PVC wastes might include units 1,2, 4,5,7,9,13,19,24. For the goal of pretreatment for discharge to municipal sewers, where the industrial wastewater is a relatively small portion of the total sewage flow (less than 20 percent), a treatment train might include units 1,2,4,5,19,24. If the objective set for the municipal or regional plant is "maximum feasible purity", specific treatment compatability studies and assessment of treated sewage effluent dissolved solids content should be made. The combined waste treatment plant must be designed to satisfactorily treat the industrial wastes to the required degree.

It must be pointed out that the suggested approach to treatment process selection is adequate only to provide a basis for order-of-magnitude estimates of alternative overall treatment disposal systems. Specific plant designs for more detailed comparisons should be based on specific wastewater characterization studies and treatability investigations.

Estimates of cost of the selected process train can be made using the data presented in Figures 1-D thru 15-D from References (4). These curves relate design capacity of the units to capital costs. They are based on data pertinent to the organic chemicals industry and are considered to be generally applicable to plastics as well. Investigations in the organic chemical industry have shown, and it is expected that similar conditions exist for the plastics industry, that treatment costs are more related to production variables than to wastewater flow variables, so caution should be employed in the use of estimates derived on generalized data and approaches. The cost estimates in Figures 1-D to 15-D are based on 1968 costs and should be extended as appropriate. The total costs representing the sum of unit costs from the curves should be increased by a factor between 1.25 and 1.45 to account for related appurtenances and other project costs. Copies of Figure 4 and Figures 1-D thru 15-D from Reference (4) are attached as is a copy of Figure 13 from Reference (3).

TABLE 3

SUMMARY OF SOME WASTEWATER CHARACTERISTICS

Product	Flow Rate Gal./1000 lbs. Prod	BOD mg/l	COD mg/L	Suspended Solids mg/L	pH
Nylon 6 [1]	300-6500	1300-4000	2800-4000	150-400	5.5-10.0
Polystyrene	250-500	1000-1600	1000-3000	100-500	-
Polyethylene					
High Density	400-720,000	120- [2]	200-335	90-	6.5-8.5
Low Density	100-1400	240-	200-4000	240-	6.5-8.5
Polyvinyl Chloride	750-2000	500-1200	700-2000	100-200	-
Polyvinyl Acetate	10,000	200-900	2000-10,000	150-2000	3-10
Polyvinyl Alcohol		No Data Available			
Butadiene-Styrene		No Data Available			

[1] Actually composite of Nylon 6 and Nylon 6,6 wastewaters-range is probably much broader

[2] Concentrations as low as 10-20 mg/L have been observed

TABLE 4

AVERAGE FLOW AND WASTE LOADINGS OF WASTEWATERS FROM VINYL POLYMERIZATION PROCESSES PER MILLION POUNDS OF PRODUCT

Product Category	Process	Flow Million Gallons	BOD_5 lbs.	COD lbs.	Suspended Solids lbs.
PVC	Suspension	1.24	200	3,200	16,000
Copolymer	Suspension	1.06	2,800	10,600	12,800
PVC	Emulsion	0.62	445	15,800	13,900
Vinyl Polymer	Not Specified	1-2	10,000	6,000	1,500

[1] Published Data for Vinyl Polymer Industry - Reference (2)

LIST OF REFERENCES

1. (Unpublished) Interim Report - Industrial Waste Study of the Plastic Materials and Synthetics Industry - EPA/WQO Contract No. 68-01-0030 - by Celanese Research Co.

2. The Cost of Clean Water - Volume III - Industrial Wastes Profile No. 10 - Plastics Materials and Resins - FWPCA Publication No. I.W.P.-10.

3. Petrochemical Effluents Treatment Practices - FWPCA Program 12020, 2/70, Contract No. 14-12-461.

4. The Cost of Clean Water and Its Economic Impact - Volume IV - Projected Wastewater Treatment Costs in the Organic Chemicals Industry - unnumbered publication of FWPCA - 6/10/68.

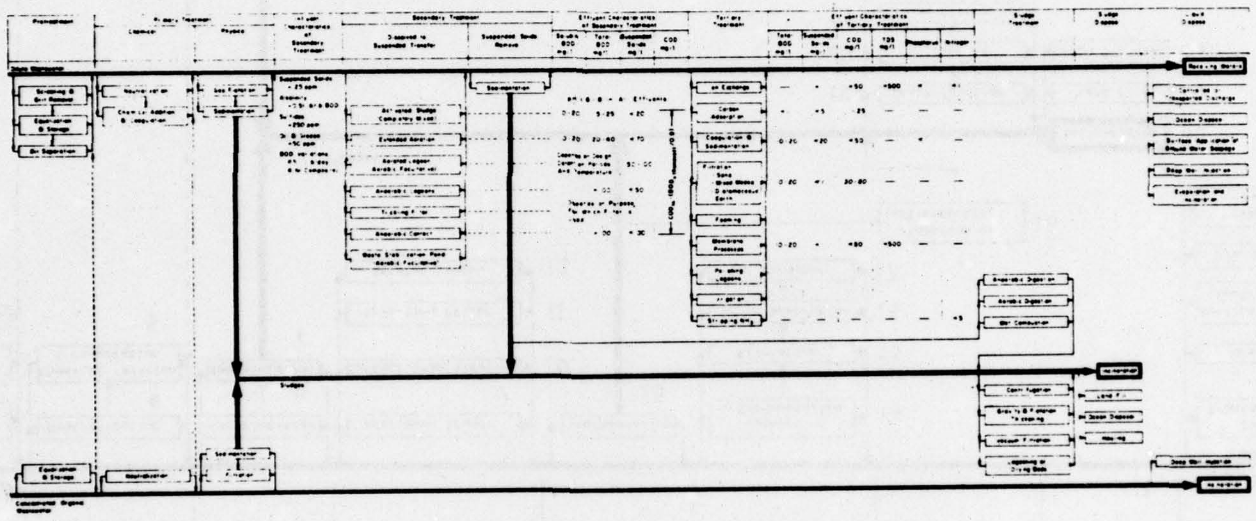
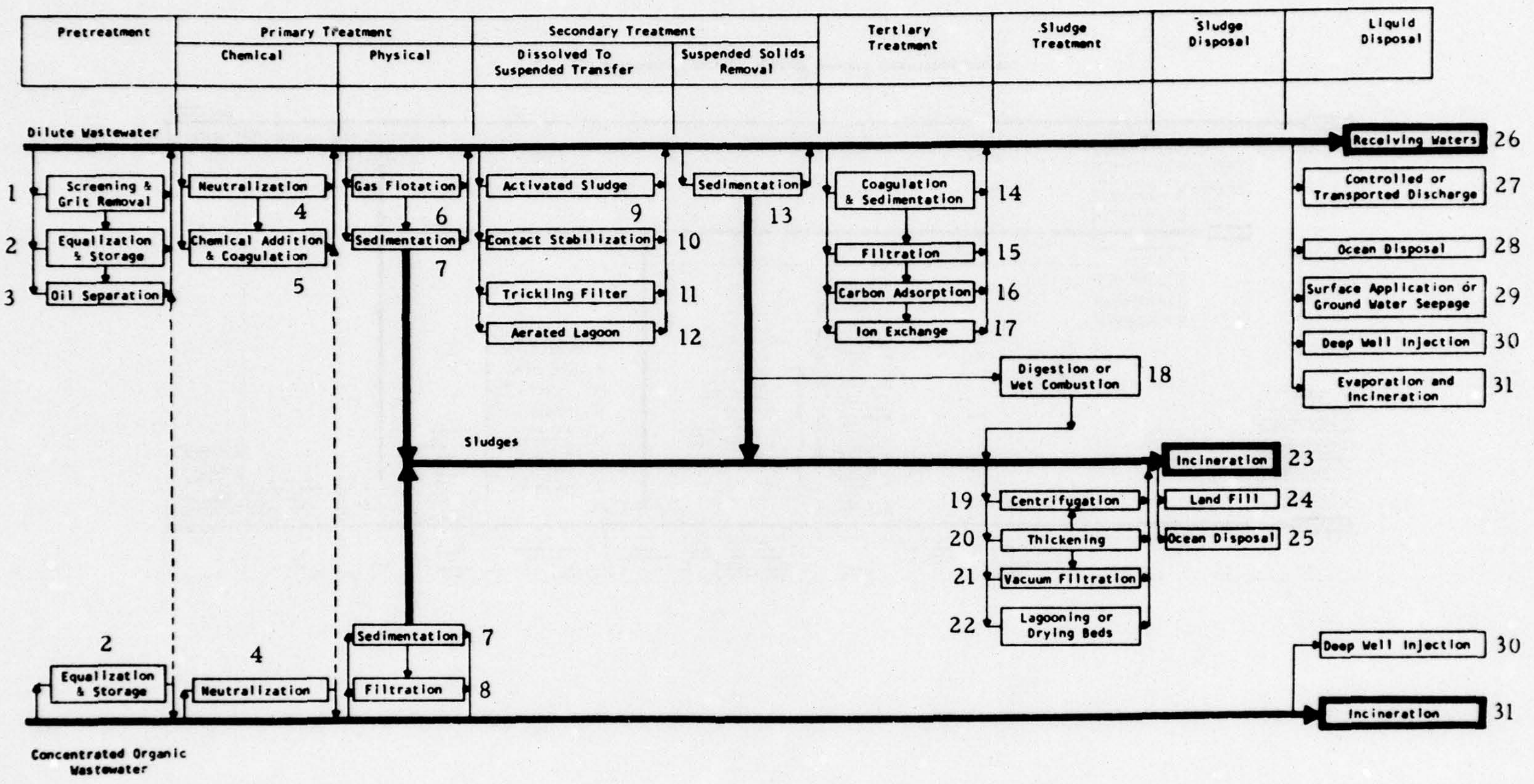


Fig 13 WASTEWATER TREATMENT SEQUENCE / PROCESS SUBSTITUTION DIAGRAM

Figure 4

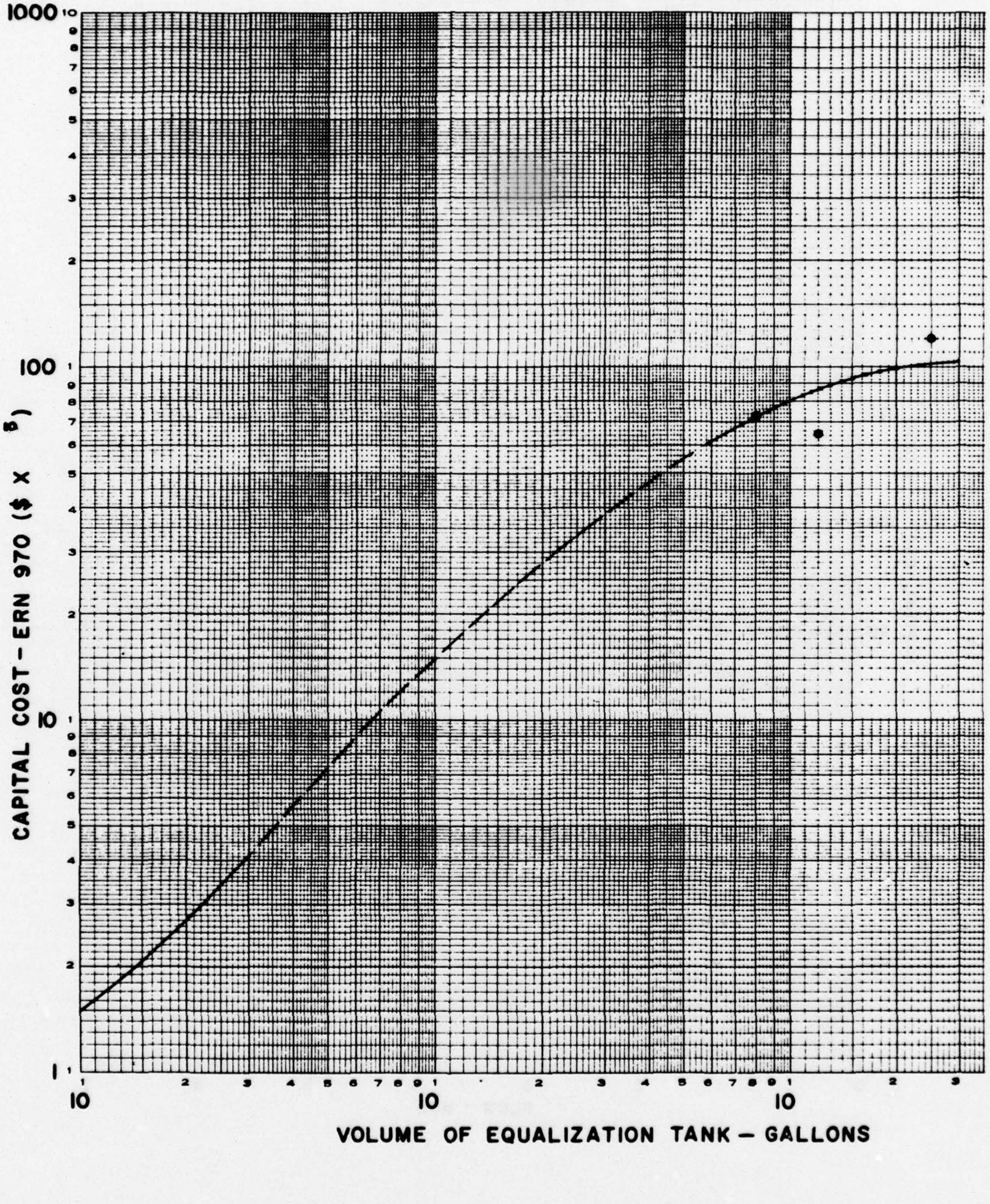
Chemical Industry

Wastewater Treatment Sequence/Processes Substitution Diagram



CAPITAL COST RELATIONSHIP
EQUALIZATION

Figure 1-D



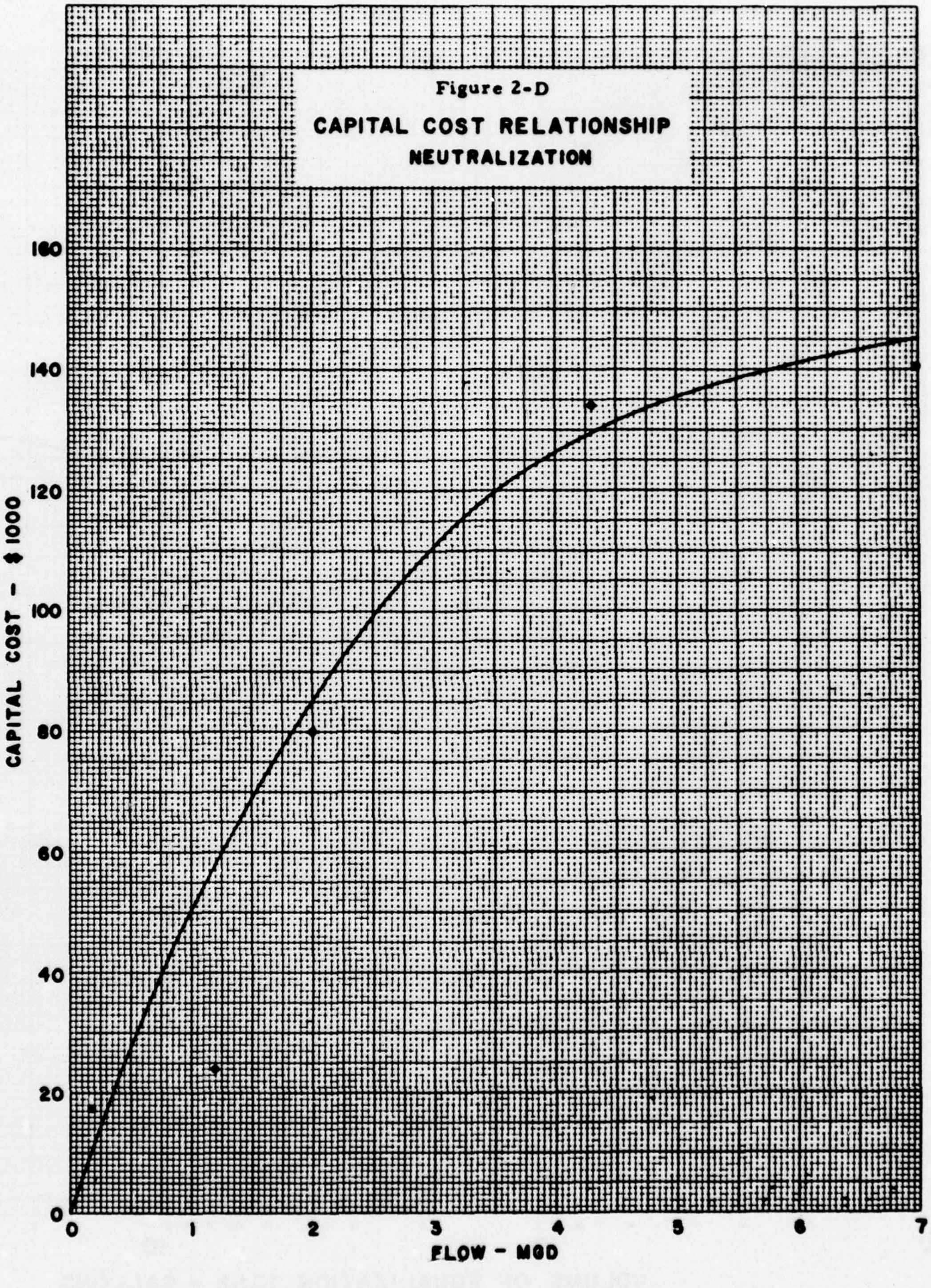


Figure 2-D

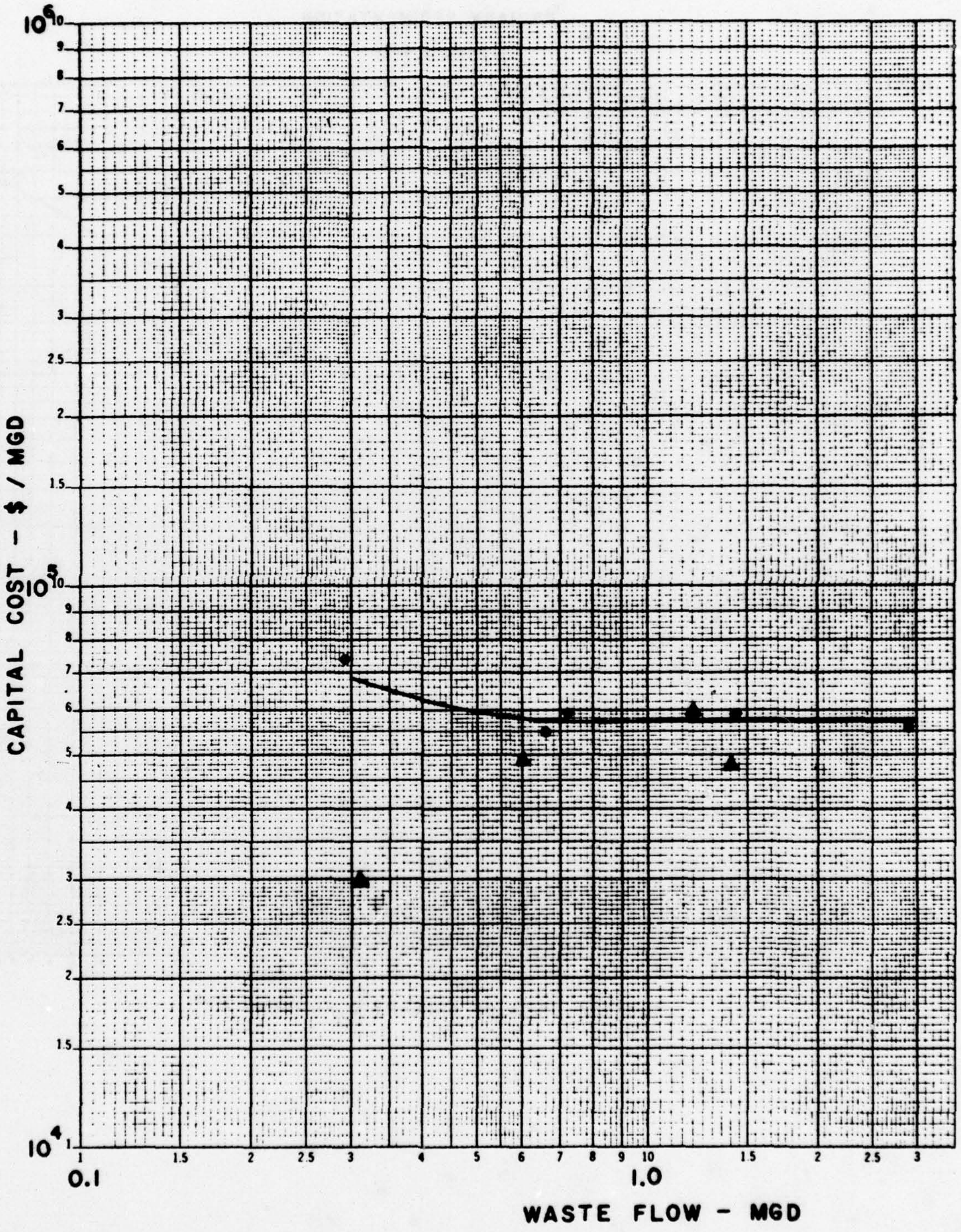
CAPITAL COST RELATIONSHIP

NEUTRALIZATION

CAPITAL COST RELATIONSHIP

OIL SEPARATION

Figure 3-D



CAPITAL COST RELATIONSHIP

PRIMARY SEDIMENTATION

Figure 4-D

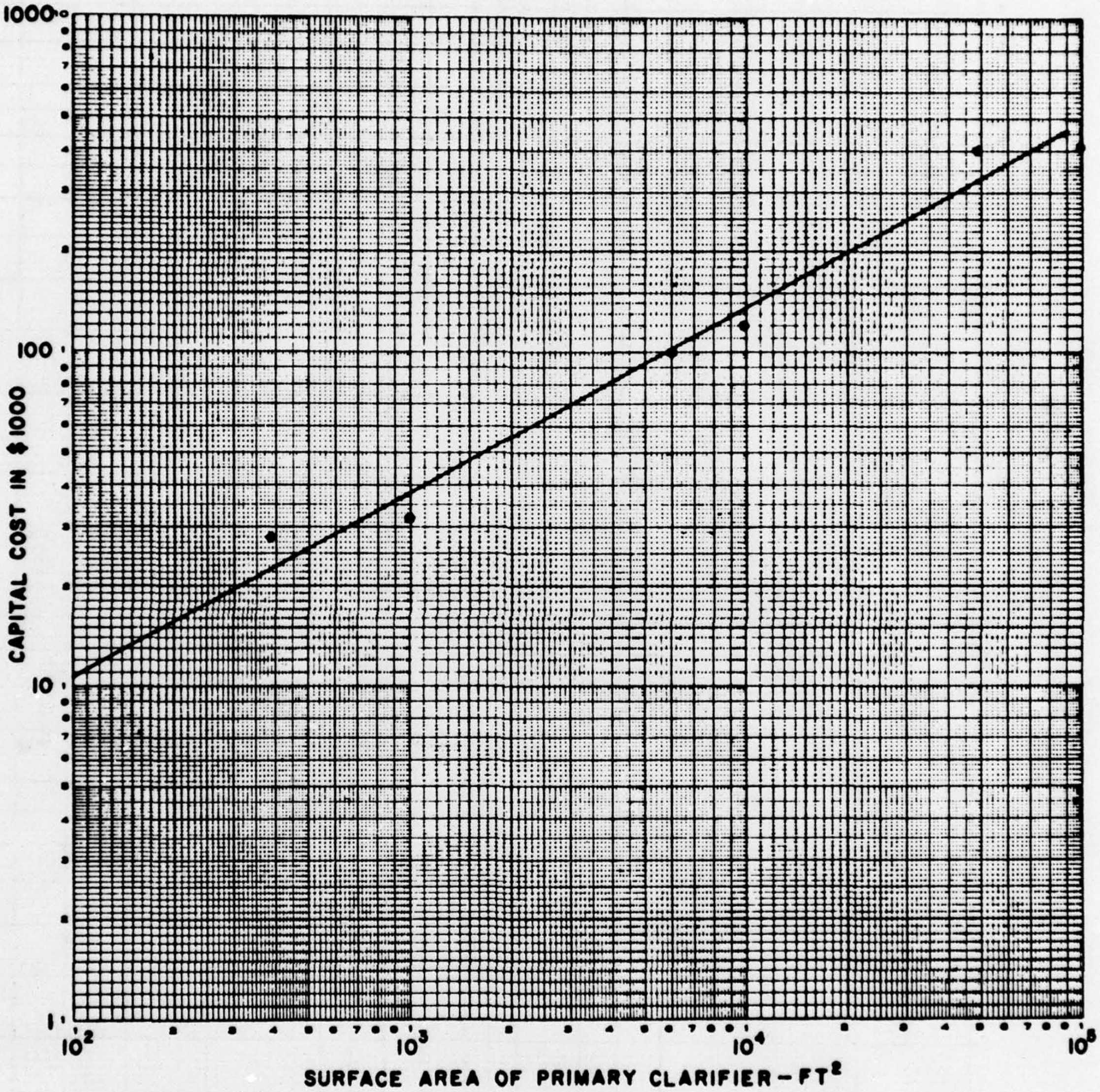
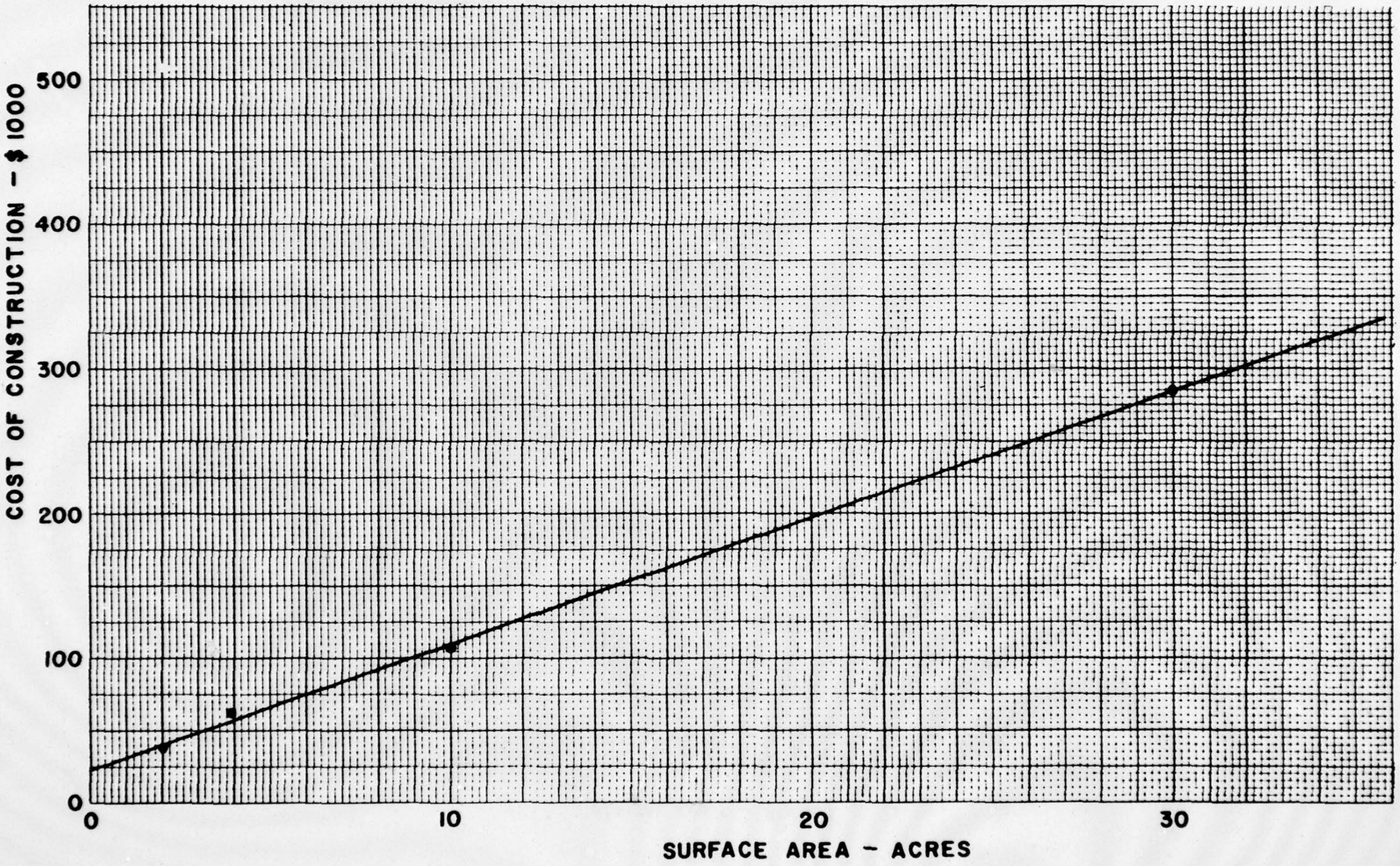


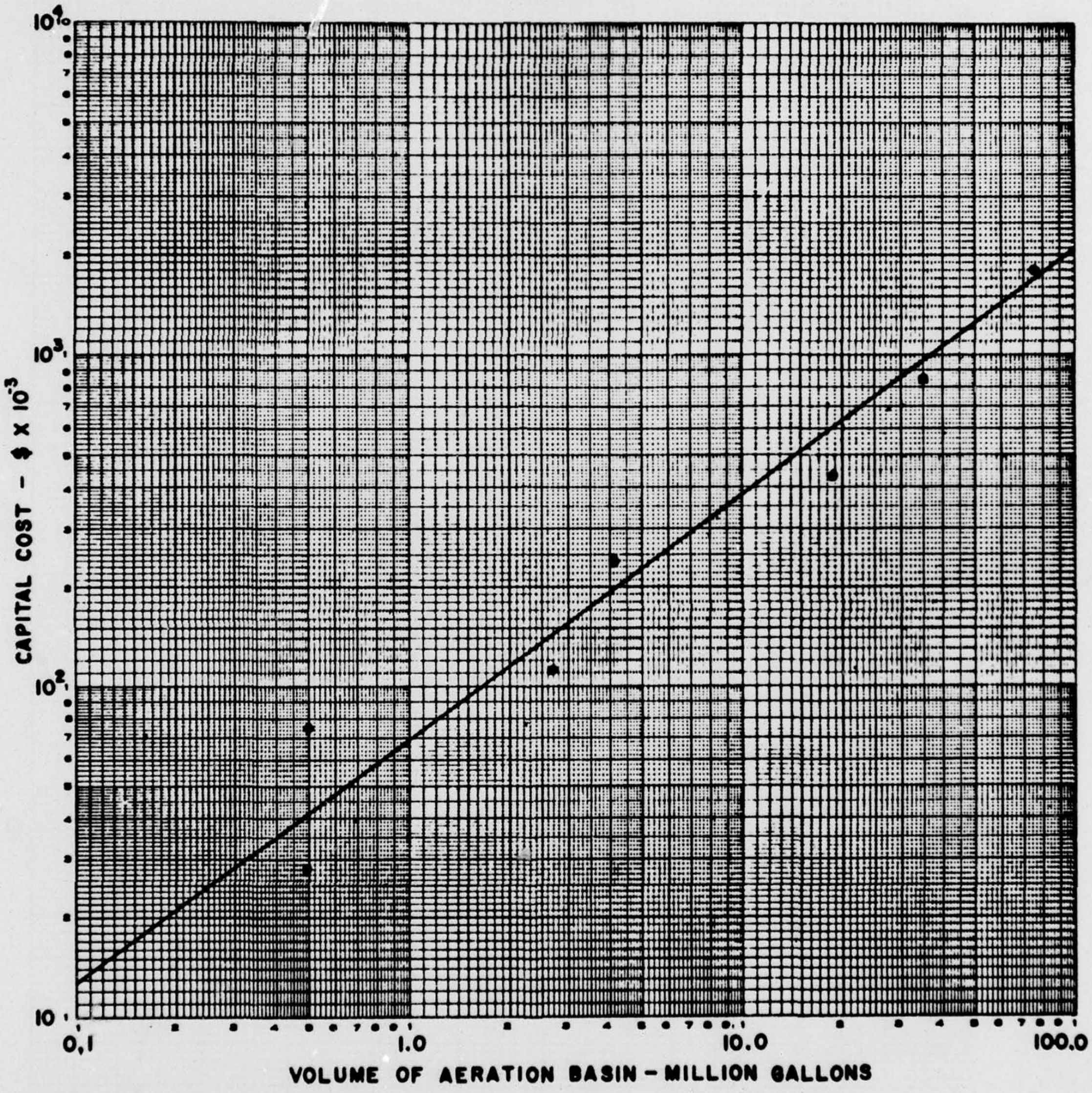
Figure 5-D

CAPITAL COST RELATIONSHIP
LAGOONS



CAPITAL COST RELATIONSHIP
AERATED LAGOON

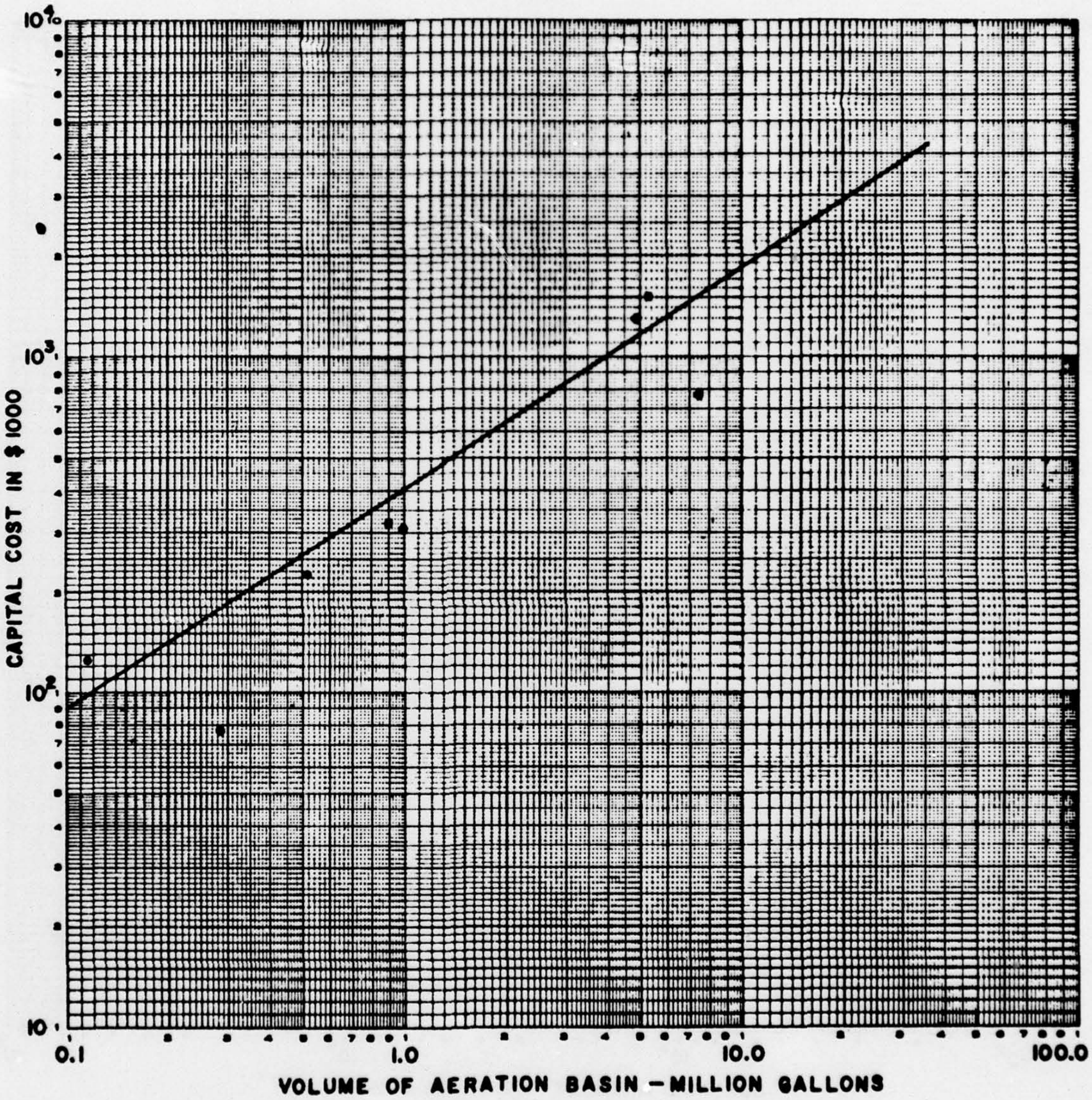
Figure 6-D



CAPITAL COST RELATIONSHIP

AERATION BASIN

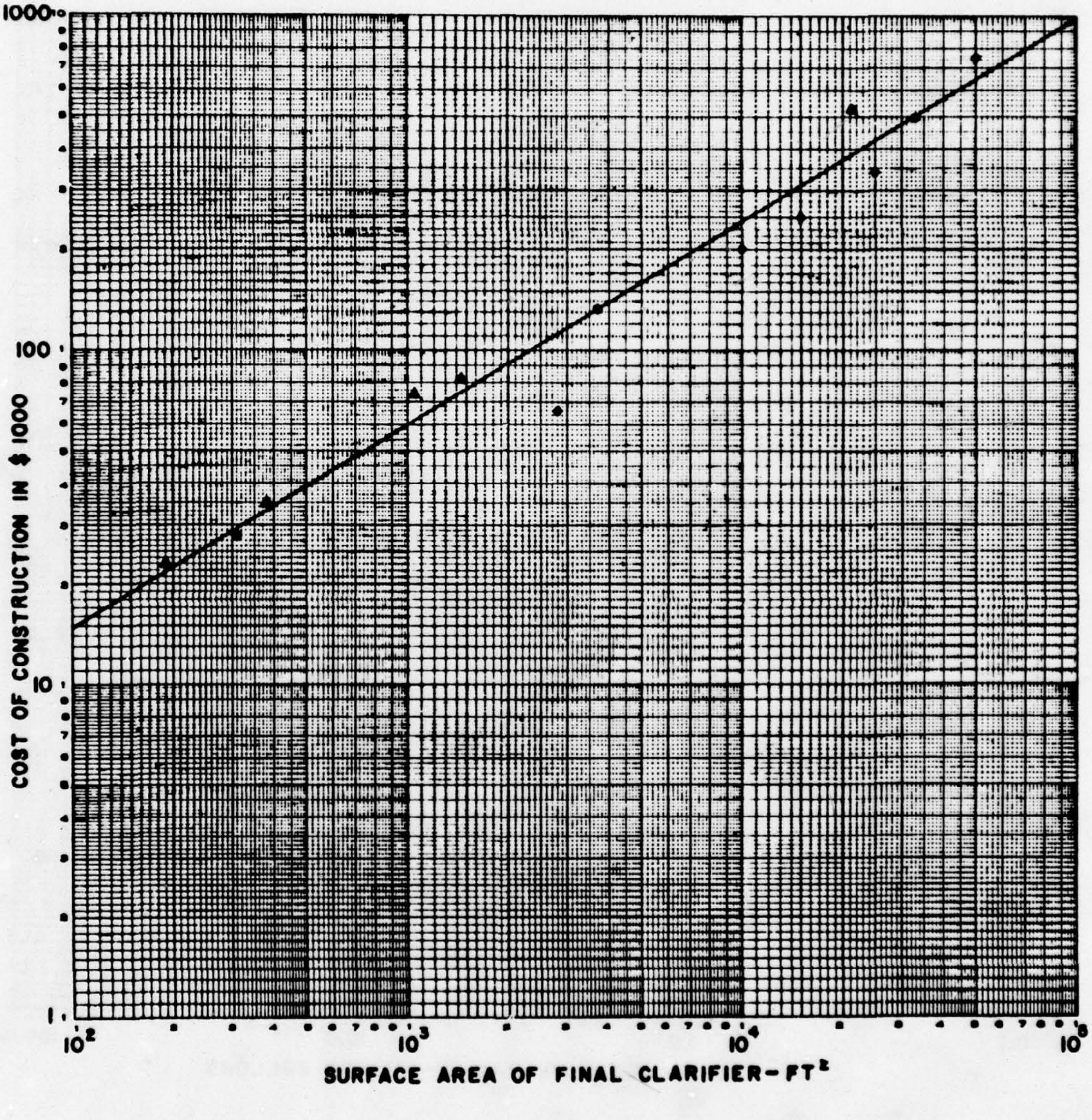
Figure 7-D



CAPITAL COST RELATIONSHIP

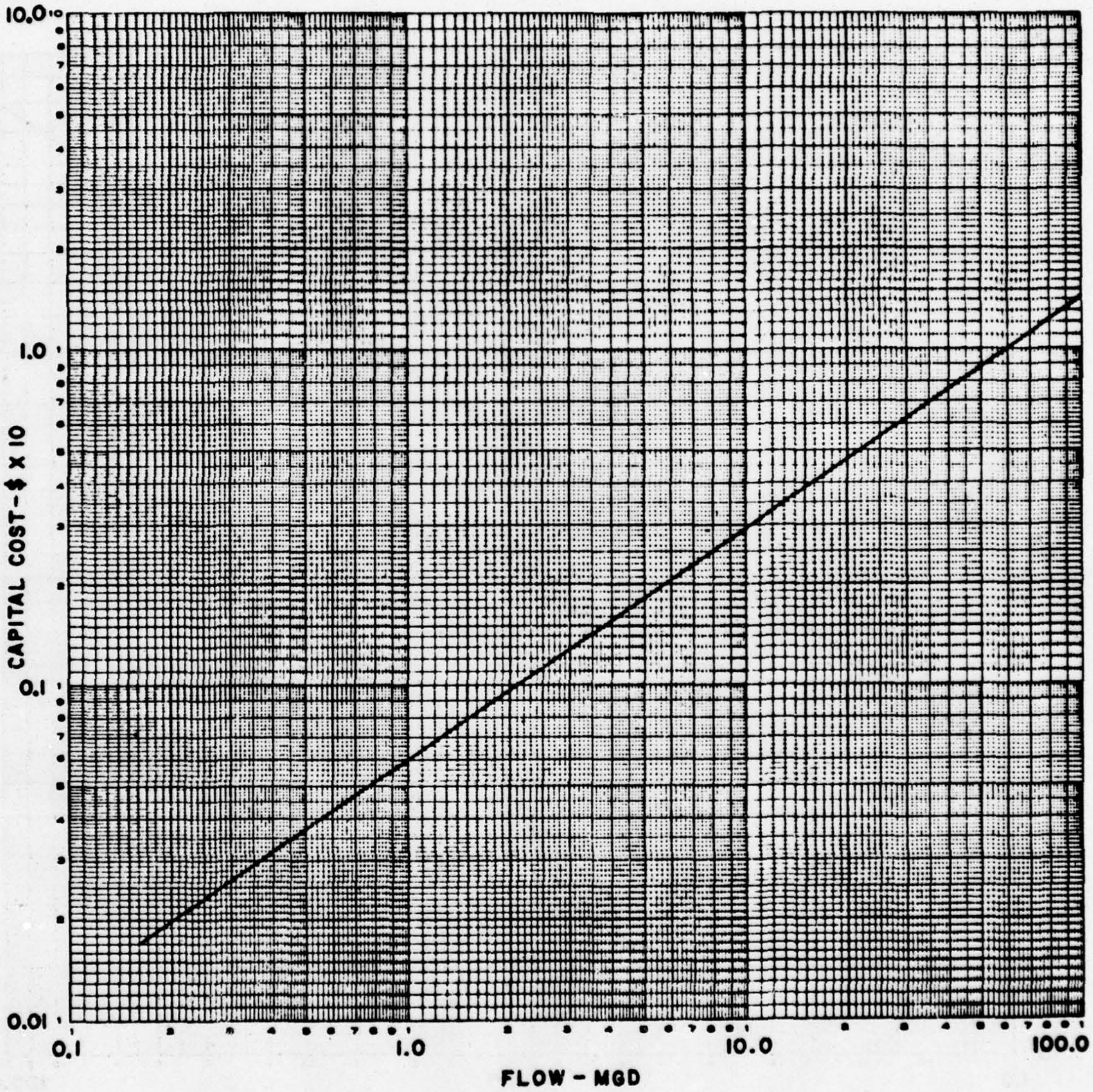
FINAL CLARIFIERS

Figure 8-D



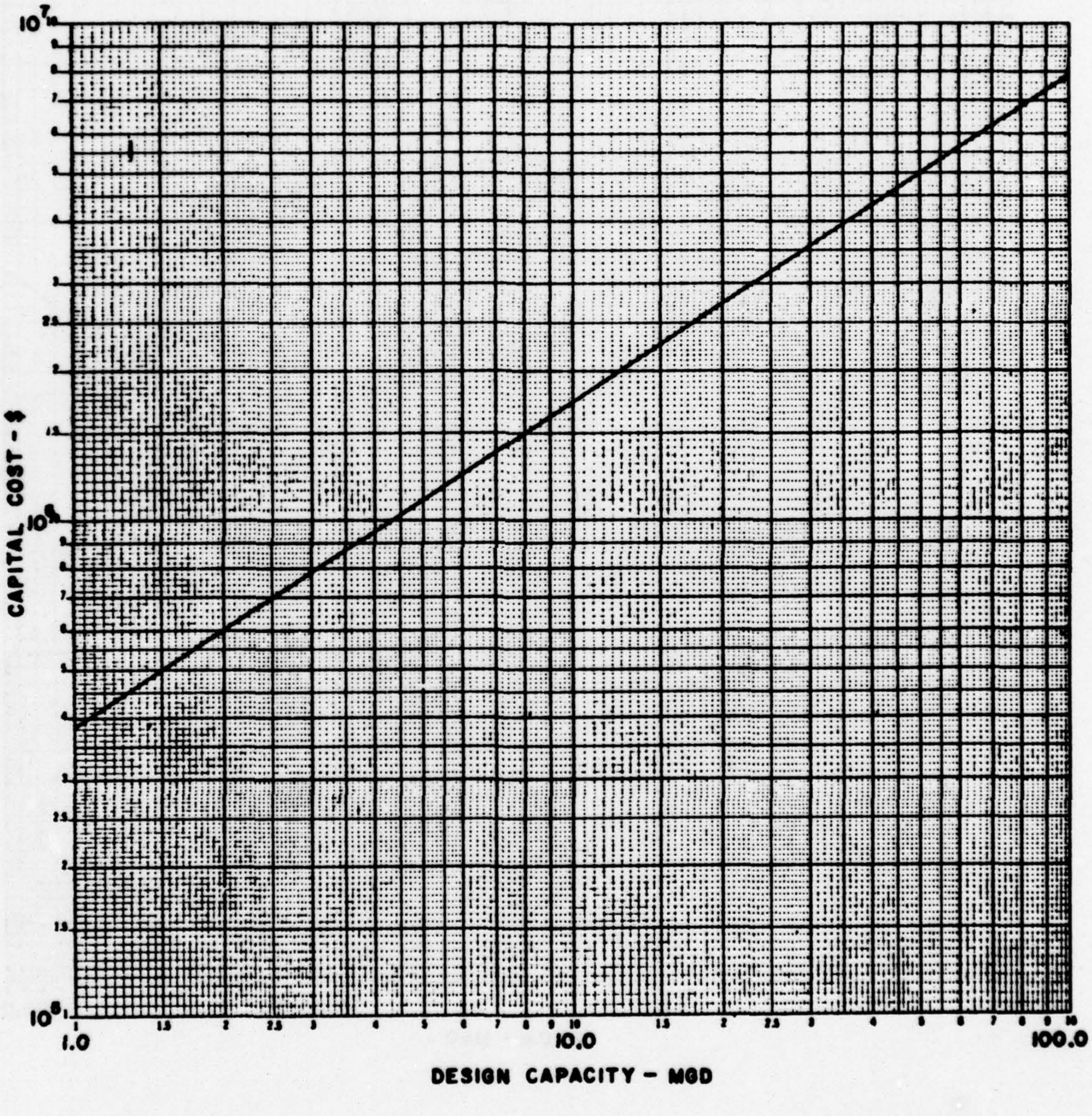
CAPITAL COST RELATIONSHIP
FILTRATION

Figure 9-D



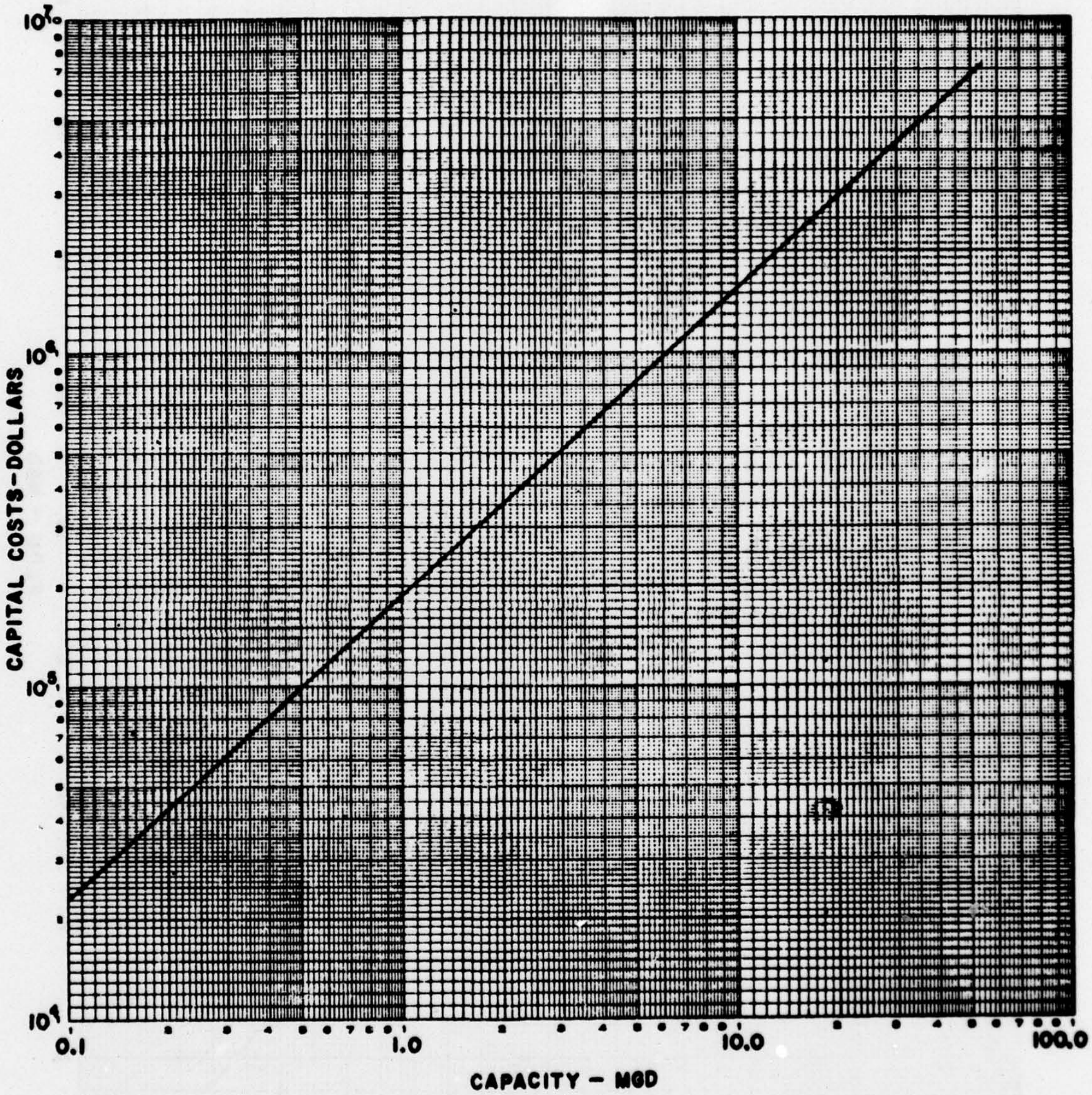
CAPITAL COST RELATIONSHIP
CARBON ADSORPTION

Figure 10-D



CAPITAL COST RELATIONSHIP
ION EXCHANGE

Figure II-D



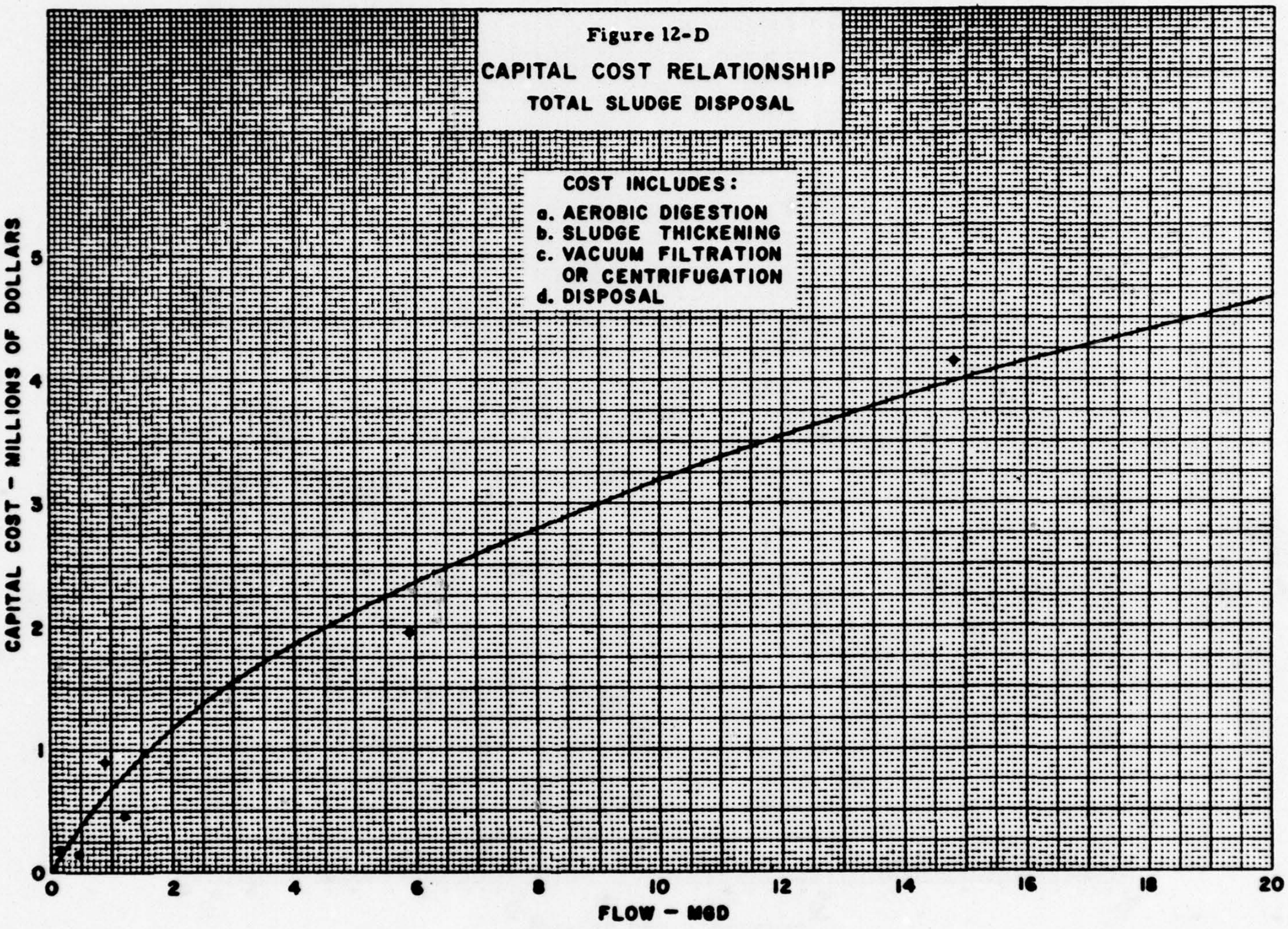


Figure 12-D

CAPITAL COST RELATIONSHIP

TOTAL SLUDGE DISPOSAL

CAPITAL COST RELATIONSHIP

FLOTATION THICKENING

Figure 13-D

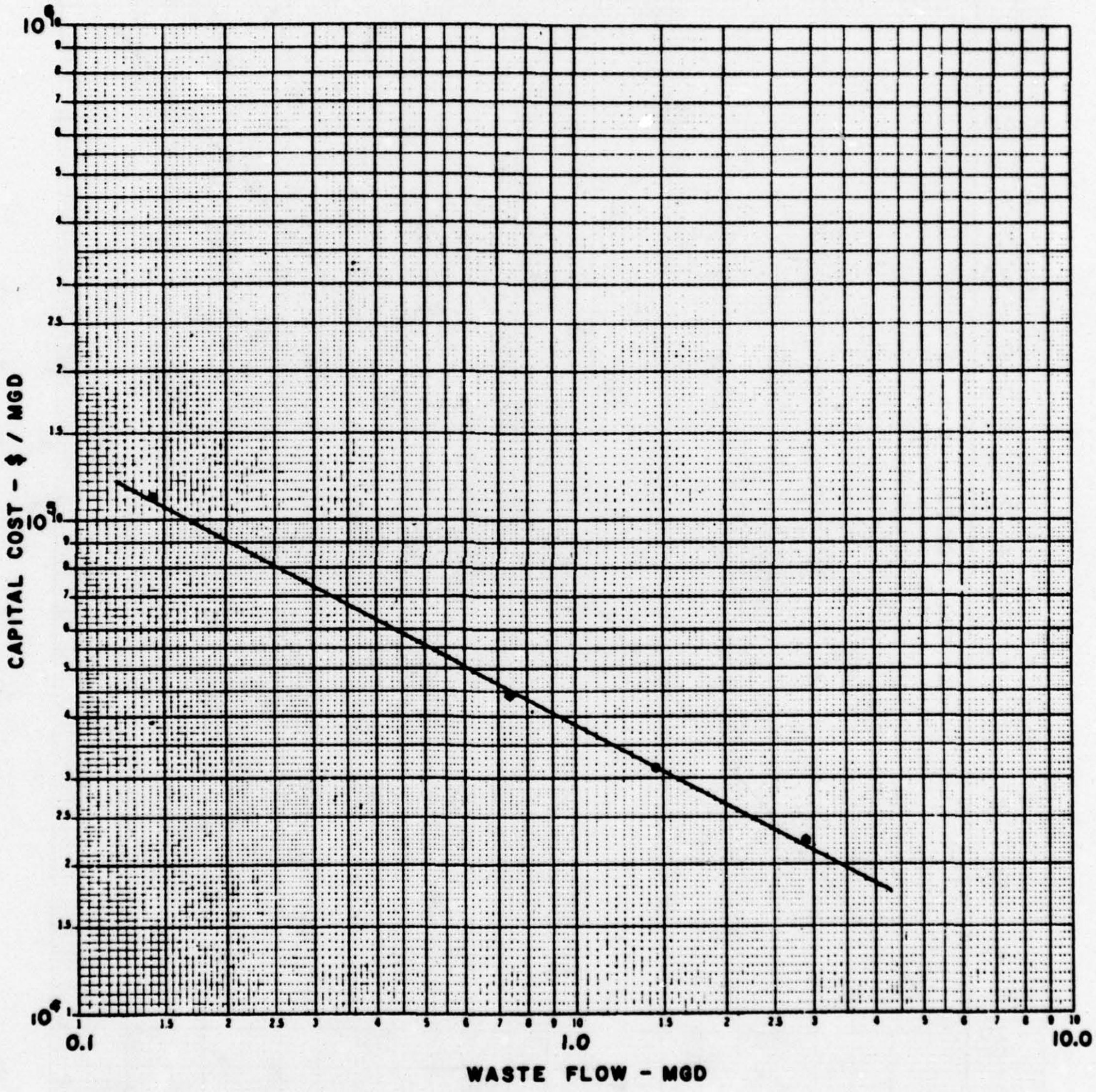
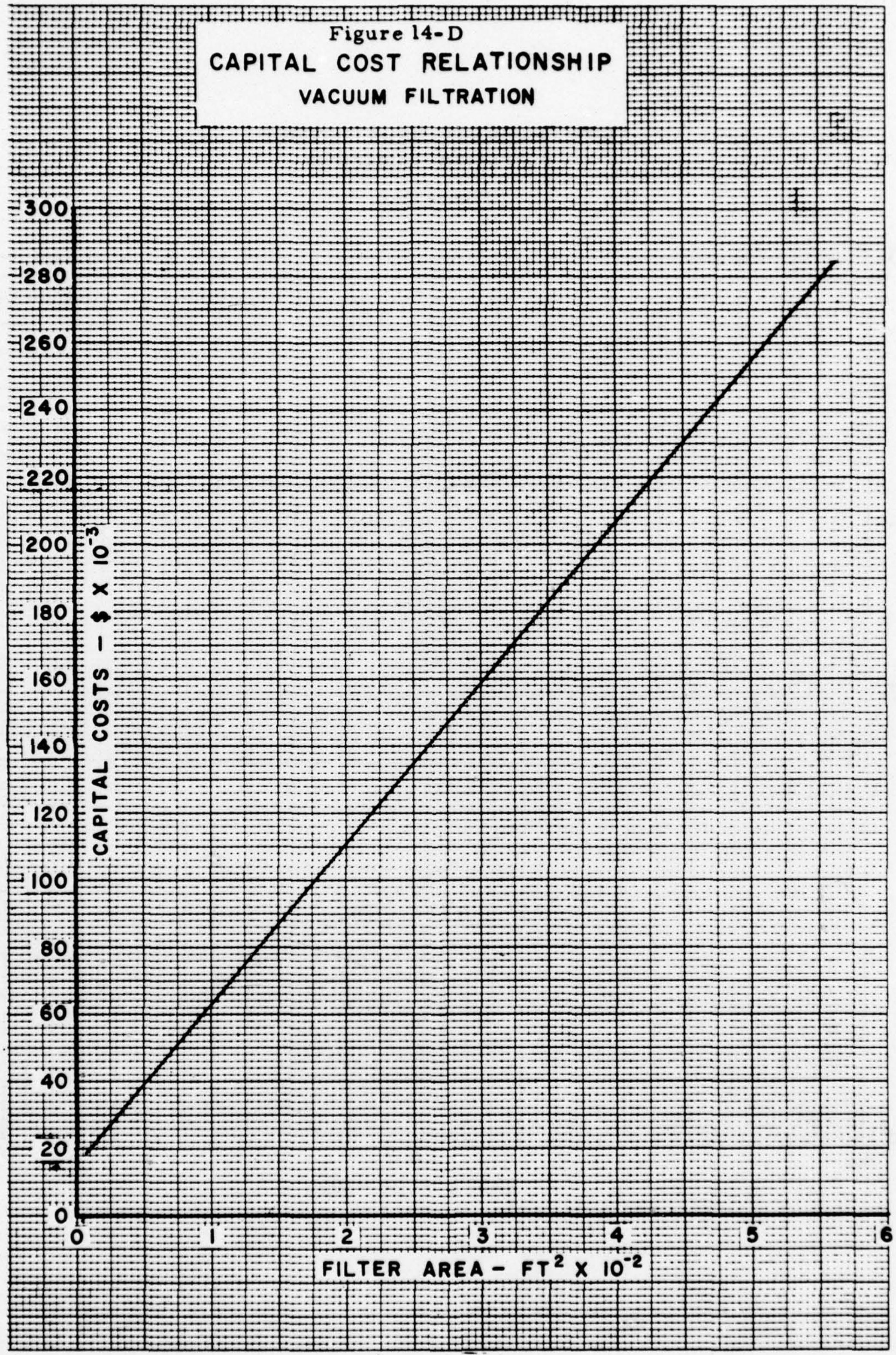


Figure 14-D

CAPITAL COST RELATIONSHIP

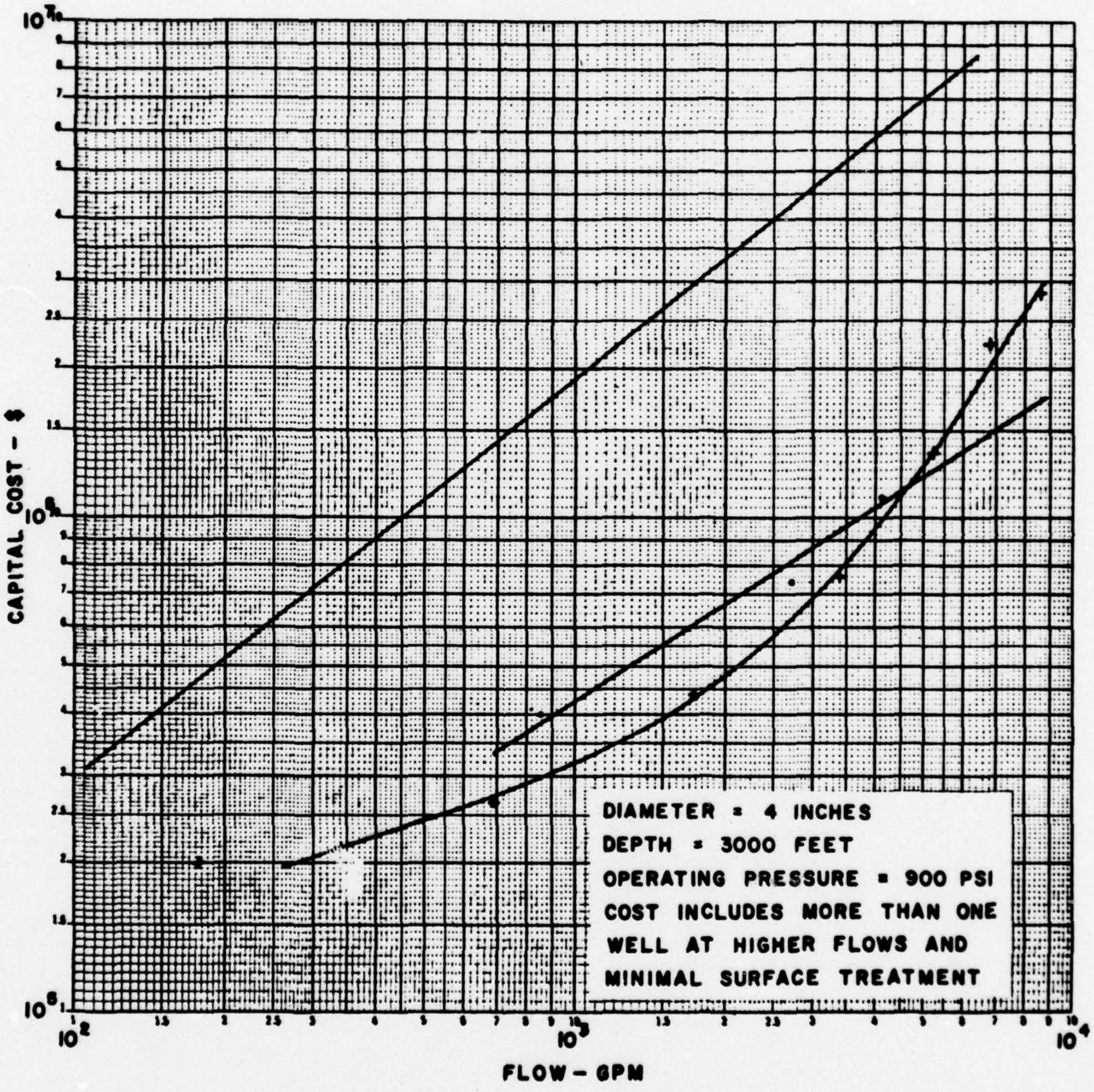
VACUUM FILTRATION



CAPITAL COST RELATIONSHIP

DEEP WELL DISPOSAL

Figure 15-D



Report to
DEPARTMENT OF THE ARMY
NORTH ATLANTIC DIVISION,
CORPS OF ENGINEERS
NEW YORK, NEW YORK
on

INDUSTRIAL WASTES PROFILE OF METAL PLATING

July 15, 1971

M&E METCALF & EDDY, INC. | ENGINEERS
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July 15, 1971

Department of the Army
North Atlantic Division, Corps of Engineers
90 Church Street
New York, New York 10007

Attention: Mr. Harry Schwarz

Gentlemen:

In accordance with the Purchase Order No. DACW33-72-M-0025 issued by the New England Division, Corps of Engineers, we hereby submit this brief report on an industrial wastes profile of metal plating.

The report was prepared by Dr. Clair N. Sawyer and Mr. Jekabs P. Vittands under the direction of the undersigned.

Respectfully submitted,

METCALF & EDDY, INC.

John Podger

John Podger
Vice President

Registered Professional Engineer
Massachusetts License No. 19130

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REPORT

INTRODUCTION

The purpose of this report is to provide a profile of metal plating wastes for use in a feasibility study for wastewater management in the Merrimack River Basin, New England.

Because of the need to complete this study within an extremely limited time period and budgetary constraints, the report constitutes a summary and evaluation of readily available information and is not a comprehensive analysis of data and research results in this field.

Metal plating wastes, unless properly treated before discharge to a stream or sewer, are extremely detrimental to the environment. These wastes are toxic to humans and aquatic life, corrosive to sewerage facilities, and disrupt biological processes customarily used in municipal and regional sewage treatment plants. Well-established technology is available for treating metal plating wastes sufficiently to eliminate their detrimental effects. More recent developments of partially closed systems are now in operation on an economic basis whereby water reuse and materials recovery are practiced.(1)

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1. All references are located at the back of the report.

CHARACTERISTICS OF WASTES

Types of Waste

The primary contaminants from metal plating processes are hexavalent chromium, sodium cyanide, cyanides of heavy metals, such as copper and zinc, soluble nickel salts, and strong acid and alkalis used in metal cleaning.

The major waste streams normally encountered are as follows:(2)

Proprietary solutions. Most metal-finishing plants use solutions which are prepared according to manufacturers' formulas. These are mainly cleaners or plating-process accelerators of various types. Exact chemical composition of the solutions should be obtained from the manufacturer.

Cyanide concentrates. This includes cyanide plating solutions and cyanide dips which contain relatively high concentrations of cyanide. Since this is one of the most toxic chemicals to both fish and other aquatic life, as well as man, its presence even in low concentrations in wastes is extremely dangerous and is to be avoided at all costs.

Cyanide rinse water originates from the rinsing of cyanide-plated or dipped metal parts.

Concentrated acid and pickling wastes originate primarily from stripping and cleaning of metal.

Strong acid rinse waters arise from rinsing following acid dips, pickling solutions, and strong acid process solutions.

Chromates originate from both plating and rinsing of metals which have been treated with chromate solutions in order to coat them with a durable protective finish. Since chromium, like cyanide, is toxic even in very low concentrations, chromium wastes are segregated and treated to remove all the chromium.

Concentrated alkalis include spent alkaline cleaning solutions - usually containing soaps, oils, and suspended solids - which are dumped periodically.

Other wastes requiring treatment. In most metal-finishing plants there are wastes which contain metal compounds, oils, soaps, and suspended solids, which can be treated by chemical precipitation and pH adjustment.

Wastewaters not requiring treatment. These include cooling water and other waters unchanged in quality, which may be discharged without treatment.

The Ohio River Valley Water Sanitation Commission (ORSANCO)(3) identifies the chemicals requiring treatment in each waste stream as shown in Table 1.

Quality of Wastes

Under present circumstances, there are wide variations in volume and concentration of wastes from plant to plant. Manufacturing practices, plant operations, availability of process and cooling water, and wastewater treatment requirements all affect the volume and composition of the final waste effluent. Because of an increasing competition for

Table 1. Characteristics of Wastes

Waste stream	Chemicals requiring treatment											
	NaCN	CuCN	ZnCN	AgCN	CdCN	Alkali	CrO_3 (CrO_4)	$CuSO_4$	$NiSO_4$	H_2SO_4	HCl	$FeSO_4$
Cyanide concentrates	x	x	x	x	x							
Cyanide rinse water	x	x	x	x	x							
Concentrated acid pickling liquors										x	x	x
Strong acid rinse water										x	x	x
Chromate wastes							x					
Concentrated alkalis						x						
Other wastes requiring treatment						x		x	x	x	x	x

water supplies, and more stringent enforcement of water pollution control criteria on a national basis, the trend is towards a greater degree of uniformity in the "standard raw waste load".

Table 2 shows a cross-section of readily available information(4) on plants that undertake metal plating on a routine basis. Waste volumes cannot be related to quantities of product manufactured on any meaningful basis because plating is a function of surface area. Quantities listed in the table therefore provide no more than a very general guide for planning purposes.

Effects of Metal Plating Wastes on Sewers

Unless sufficiently diluted, plating wastes are corrosive to sewer structures. Table 3 shows limiting concentrations that should be discharged to sewers.

Effects of Metal Plating Wastes on Treatment Processes at Municipal and Regional Plants

The effect of wastes on conventional treatment processes at municipal and regional plants depends on the concentration and degree of toxicity of the wastes and on the treatment processes employed at the plant.

In general, detrimental effects can be characterized as follows. The metal content of wastes precipitating out in the sedimentation process may overtax the sludge handling capacity of the plant. Toxic metals, unless sufficiently diluted, impair or halt bacteriological processes involved in

Table 2. Volumes of Chromium and Cyanide-Bearing Untreated Wastes from Typical Plating Operations in the Electroplating Industry

	Chromium-Bearing Waste				Cyanide-Bearing Waste				
		Analyses, ppm(1)				Analyses, ppm(1)			
Type of Work Plated	Volume gal.	Cr	Ni	Cu	Volume gal.	CN	Cu	Zn	Cd
Aircraft engines and parts	440,630/day	--	--	--	293,760/day	--	--	--	--
Automogile bumpers	480,000/day	--	--	--	--	--	--	--	--
Automobile grills	100,000/day	700	--	--	--	--	--	--	--
Missile parts	80,000/day	1	--	--	32,000/day	80	--	--	--
Office furniture	24,000/day	--	--	--	--	--	--	--	--
Typewriters and office machines	50,000/day	16	39	--	--	39	--	--	--
Instrumentation and control equipment	--	--	--	--	13,000/day	--	--	--	--
Electronic hardware	828,000/day	--	--	--	259,200/day	200-1500	--	--	--
Home appliances	43,200/day	--	--	--	108,000/day	--	--	--	--
Television antennaes	--	--	--	--	11,000/day	--	--	--	--
Silverware	40,000/day	5	33	135	165,000/day	172	18	11	--
Instrument motors and electric clocks	112,000/day	--	---	--	--	--	--	--	--
Automobile manufacture	620,000/day	30	80	70	410,000/day	204	--	113	--
Unspecified		--	--	--	250-400/hr	40-130	--	--	--
Metal fastener plant	89,000/day	52	302	--	--	--	--	--	--

1. Analyses not shown are not available.

Table 3. Some Restrictions on Plating and Metal Finishing Wastes Discharged to Sewers(1)

	pH	CN	Cu	Cr^6	Cd	Zn	Ni	Ba	Other Heavy Metals	Total Dissolved Solids	Suspended Solids	Ref.
Typical Limits	6-10	0	0.3	0.05	0.4	0.3	2.0	-	-	-	-	3
Typical Range	5-10	0.2	0.4	0-10	0-5	0-5	2-10	-	0-50	2000-5000	200-1000	3
Massachusetts	7-9.5	0.0	0.5-1	0.0	0.5	1	1	-	-(4)	350	15	-(2)
MDC	5.5-9.5	0.0	0.5	0.5	0.1	0.5	0.5	0.5			500	-(3)

1. All units are in ppm except for pH.
2. Restrictions shown for Massachusetts are unofficial guidelines used by the Massachusetts Division of Water Pollution Control.
3. Used as criteria by the Boston Metropolitan Sewer District.
4. As limited by municipal ordinances.

sludge digestion and secondary treatment. Table 4 shows the concentrations and related effects of some of the important troublesome items.(4) The activated sludge process reportedly can tolerate greater influent metal concentrations than the anaerobic sludge digestion process.(5)

"In practically all instances when metals cause digester troubles copper, zinc, nickel, chromium, and cadmium are involved... The effects of the metals are additive and gasification will be lowered slightly when their concentration reaches 200 to 400 mg/L in raw sludge (0.4 to 0.8 percent on dry solids basis) if the sulfate concentration in sewage is low. Concentrations of 1,000 mg/L (2 percent dry basis) will cause gasification to cease in two to three weeks if dose is continued."(5)

Effects of Metal Plating Wastes on Receiving Waters

Cyanides and metal salts, even in low concentrations, are destructive to aquatic life. Table 5 shows the lowest concentrations which are lethal to fish. Guidelines used by the Massachusetts Division of Water Pollution Control for permitting waste discharges to receiving waters are also shown in the table.

Effects of Metal Plating Wastes on Domestic Water Supplies

The Merrimack River is presently used as a source of domestic water supply and there is a considerable potential for its further development. Requirements for industrial and domestic waste discharges should therefore be based on

Table 4. Effects of Metal Plating Wastes on Sewage Treatment

	Tolerable Concentration at Steady Flow ppm	Concentration with Appreciable Effect at Steady Flow ppm	Concentration of "Slugs" Causing Temporary Impairment ppm	Concentration of "Slugs" Causing Considerable Impairment ppm
Hexavalent Chromium				
Trickling filter	1-4	10		
Activated sludge	2-8	5-10	10-50	100-500
Trivalent Chromium				
Trickling filter				
Activated sludge				
Copper				
Trickling filter		1-3		
Activated sludge	1	4(1)	50	
Zinc				
Trickling filter		1-3		
Activated sludge		5-10		
Cadmium				
Trickling filter				
Activated sludge				
Nickel				
Trickling filter				
Activated sludge		1-3		
Cyanide				
Trickling filter	2		30	
Activated sludge	1-2	9(1)		
Acid				
Trickling filter				
Activated sludge				
Solids				
Trickling filter				
Activated sludge				

1. Combination of 9 ppm CN and 4 ppm Cu adversely affected sludge flocculation.

Table 5. Concentration of Cyanides and Metal Salts Fatal to Some Fish and Limiting Concentrations for Discharges into Streams(6) (7)

Component	Concentrations Fatal to some fish, ppm	Limiting Concentrations for discharges in Massachusetts, ppm
pH	-	7.0 to 9.5
Hexavalent chromium	5	0.0
Trivalent chromium	about 5	-
Total chromium	-	0.5
Cyanide	0.05	0.0
Ferrocyanide	1.45	-
Copper	0.02	0.5-1
Zinc	0.3	1
Cadmium	0.6	0.5
Nickel	5	1

maintaining and improving the river's potential as a source of domestic water supply. Table 6 shows limiting concentrations of selected chemical substances in water supply sources as recommended by the U. S. Public Health Service. Also shown are levels which constitute grounds for rejection of a water supply.

Table 6. Selected U. S. Public Health Service Drinking Water Standards(8)

Component	Recommended Maximum Level, ppm	Levels for Rejection, ppm
Arsenic	0.01	0.05
Barium	--	1.0
Chloride	250	--
Copper	1.00	--
Cyanide	0.01	0.2
Iron	0.3	--
Cadmium	--	--
Nickel	2.0	--
Sulfate	250	--
Tin	1.0	--
Zinc	5.0	--
Hexavalent chromium	--	0.05
Trivalent chromium	--	1.0
Lead	--	0.05
Silver	--	0.05

CONVENTIONAL WASTE TREATMENT PRACTICES

The objective of plating waste treatment operations is the removal of cyanides, chromium, and all other metals.

Batch versus Continuous Treatment

Metal plating wastes may be treated as a continuous flow process or may be collected in tanks and treated in a batch operation.

Batch treatment operations are generally suitable for smaller plants where intermittent storage of wastes is feasible. Batch operations provide better control over the treatment and discharge of wastes, require less chemicals, and provide better equalization where manufacturing processes involve slug discharges.

Continuous flow treatment permits handling of larger waste flows for the sizes of facilities involved and is easier to control automatically. However, automatic control is difficult and various checks and safety precautions must be provided to protect the receiving waters.

Methods of Treatment

Cyanides and chromates can be treated more easily when separated. The most common methods of treating metal plating wastes are on this basis.

The treatment of cyanides can be accomplished by at least 10 methods(3): chlorination, hypochlorites, chlorine dioxide, ozonation, conversion to less toxic cyanide complexes, electrolytic oxidation, acidification, lime-sulfur method, ion exchange, and heating to dryness. The most commonly used method is the destruction of cyanide by chlorine gas or by hypochlorites.

Chromium wastes may be treated by a variety of reduction methods followed by precipitation or by ion exchange. The former method is used most commonly for treatment.

The removal of other metals is usually accomplished by neutralization to pH 8.5 under which conditions they are precipitated as hydroxides.

Conventional Treatment of Metal Plating Wastes

Figure 1, reproduced from Reference No. 3, shows a waste flow schematic for the most common treatment process.

Cyanide Destruction. Treatment involves the addition of alkalinity, usually caustic soda, to raise the pH to about 11. Oxidation by the addition of chlorine is then accomplished. To insure complete destruction of cyanide, violent agitation must accompany the chlorination. About 6 lbs. each of caustic soda and chlorine are required to oxidize 1 lb. of cyanide.(3) Conversion of cyanide to cyanate is rapid but about 24 hours are required to complete the process.(3) For this reason, the process usually involves two steps: oxidation at pH 11 followed by lowering of pH to 8 and further addition of chlorine to convert cyanates to nitrogen and CO_2. In this way the time required for completion of the process is reduced to under an hour.

Chromium Reduction and Precipitation. This treatment involves reduction of the toxic hexavalent chromium in the waste to its trivalent stage using reducing agents such as sulfur dioxide, sulfites, or ferrous sulfate. To insure complete reaction a pH of 3 or lower is necessary. This is accomplished by the addition of sulfuric acid. After reduction is completed lime slurry is added to raise the pH and precipitate the trivalent chromium. One ppm chromium requires about 16 ppm of copperas, 6 ppm of sulfuric acid, and 9.5 ppm of lime; producing about 2 ppm of chromic hydroxide and 0.4 ppm ferric hydroxide sludges as well as 2 ppm calcium sulfate.(3)

Neutralization and Precipitation of Metals. Usually precipitation of metals in reduced and oxidized cyanide wastes is carried out together with precipitation of other metals carried in acid and alkaline wastes. This is shown on Figure 1. Normally, lime slurry is added to neutralize and precipitate the metals.

Disposal of Sludge. Two methods are usually used for sludge disposal. Where space permits, sludge is pumped to lagoons for dewatering and settling. The liquid is not toxic and may be discharged to a water course. Dried sludge normally is excavated and hauled away to a disposal site.

Another method of sludge disposal is thickening, vacuum filtration and hauling to a disposal site.

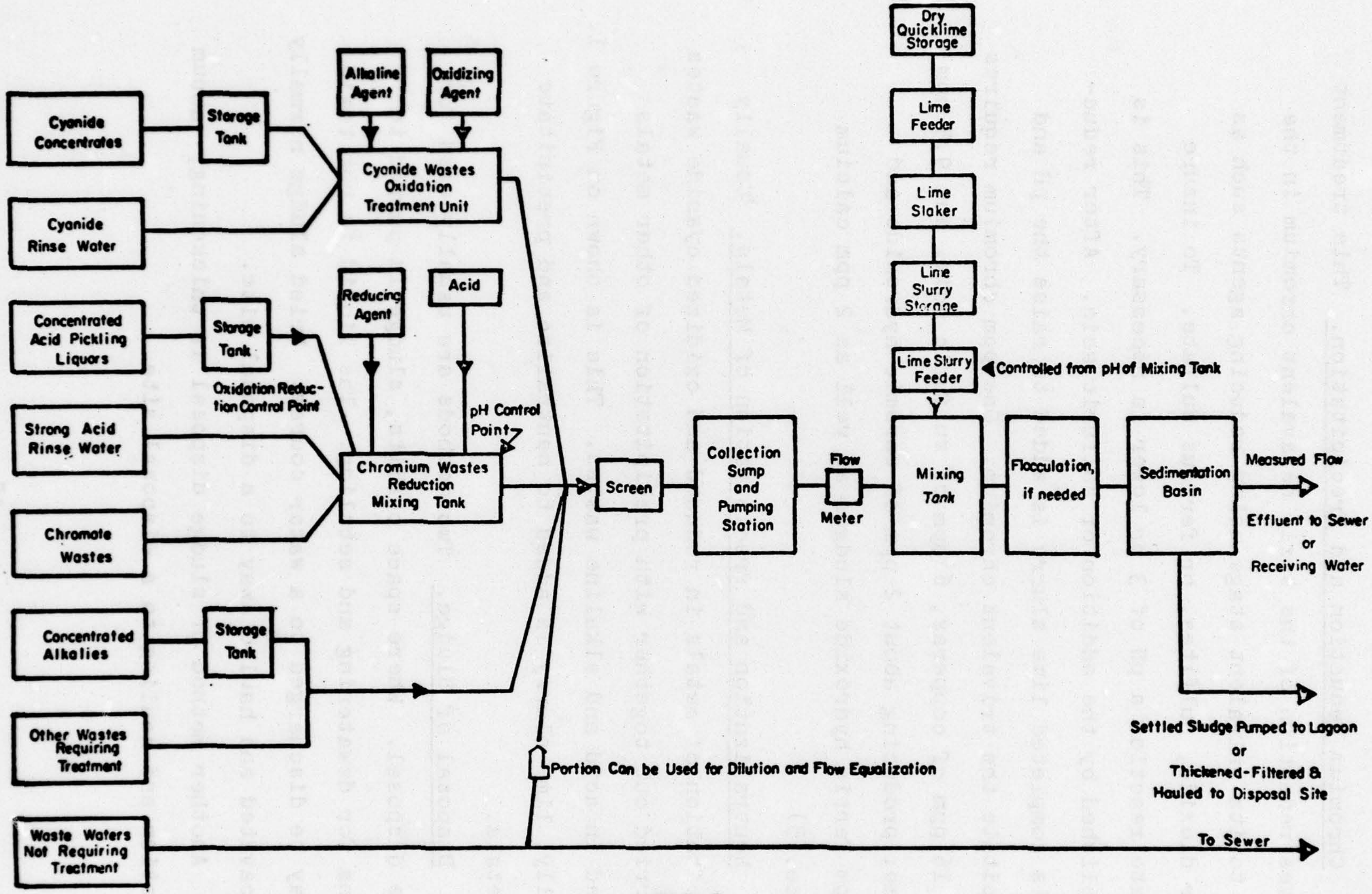

Fig. 1

CONVENTIONAL TREATMENT OF METAL PLATING WASTES

CURRENT DEVELOPMENTS IN WASTE TREATMENT

Under free enterprise economic systems, man is constantly seeking better and, hopefully, more economical ways of accomplishing desired objectives. The wastewater treatment field is no exception. In the metal plating industry accepted practices of -

1. cyanide destruction
2. chromate reduction
3. chemical recovery, and
4. solids handling

are being challenged, continually.

Cyanide Destruction

Spent Baths. In the past, spent plating baths have been stored and then discharged at controlled rates into treatment facilities for rinse waters. The major part of the cyanide in such wastes can be destroyed by electrolytic oxidation. Residual cyanides must be destroyed by conventional methods used for rinse waters. Although there is some saving in chemicals, power requirements are high and several days treatment time is required.

The cyanide in spent baths can be destroyed also by mixing with waste chromic acid when available. This method requires that copper ion be present as a catalyst and chromic acid must be used in excess. The resultant mixture must be passed to a chrome reduction facility to destroy the excess chromates.

Integrated System. In properly designed new plants or in some old plants, it is possible to use the proprietary "Integrated System", often referred to as the "Lancy System". In this, at least two rinse tanks must be employed as shown on Figure 2 and space must be available for the chemical supply tank. The first rinse tank is actually a chemical treatment bath in which alkaline hypochlorite is recirculated and accomplishes destruction of the cyanides. The second is a true rinse tank which removes the chemical treatment solution. The effluent from it contains traces of cyanides, cyanates, and metal ions. Normally, it is suitable for direct discharge to a municipal sewer system but may not be suitable for direct discharge to a stream.

In the integrated system, spent baths must be treated separately or metered to the chemical tank.

Ozone. Ozone has been promoted as an oxidant for destroying cyanides. One plant, that of the Boeing Company at Wichita, Kansas, has been in successful operation since 1958. There appears to be no trend towards using ozone for this purpose. The use of ozone appears to be limited to very large plants.

Peroxide. A proprietary process (Kastone) has been successfully applied to the destruction of cyanide in rise waters from zinc and cadmium plating of ferrous metals. Zinc

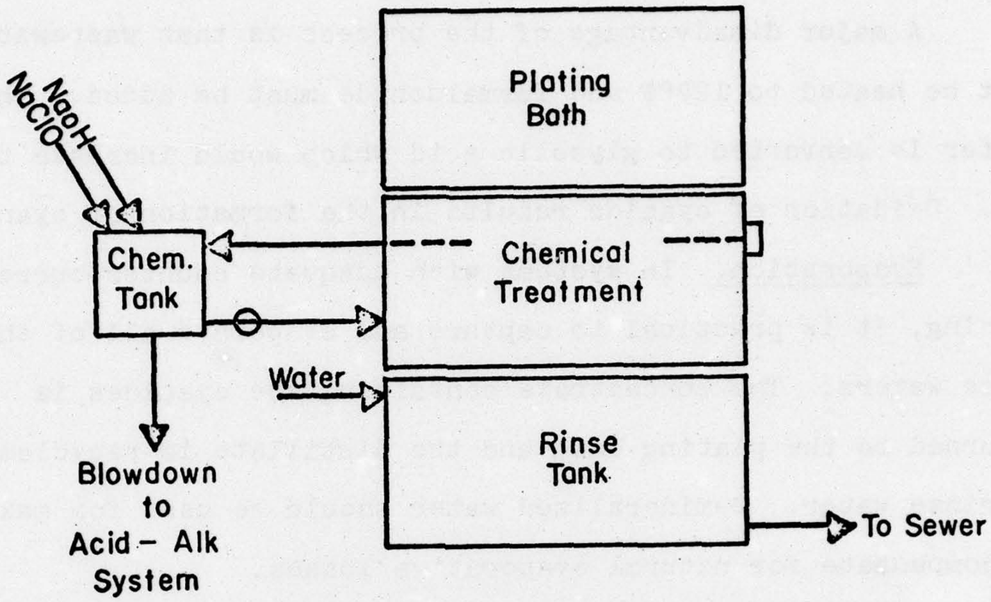

Fig. 2

INTEGRATED SYSTEM FOR IN-LINE

DESTRUCTION OF CYANIDES

and cadmium are precipitated simultaneously and can be removed by simple filtration. Kastone contains 41 percent hydrogen peroxide with a small amount of a patented catalytic compound, which aids in decomposing metal cyanide complexes.

A major disadvantage of the process is that wastewaters must be heated to 120°F and formaldehyde must be added. The latter is converted to glycolic acid which would increase the BOD. Oxidation of cyanide results in the formation of cyanate.

Evaporation. In systems with adequate counter-current rinsing, it is practical to capture and evaporate all of the rinse waters. The concentrate containing the cyanides is returned to the plating bath and the distillate is recycled as rinse water. Demineralized water should be used for makeup to compensate for natural evaporative losses.

Ion Exchange. Although ion exchange was considered a promising method of cyanide removal from rinse waters more than 20 years ago, it has not become an accepted method, mainly because the exchange process serves solely to concentrate, not destroy.

Chromate Reduction

Spent Baths. At least two schemes of treatment are proposed which will reduce the amount of chromic acid plating liquor requiring disposal by the usual reduction method.

Cation exchange can be used as a purifier to remove contaminant metals from plating and anodizing baths. This requires dilution with water before exchange and evaporation to reconcentrate the chromic acid for reuse.

Anion exchange can be used to reclaim chromates from spent baths. This scheme is practical in situations where anion exchange is used to remove chromates from rinse waters.

A new method of disposal involves reduction of chromates in spent baths by addition of spent cyanide baths, as discussed above under cyanides. Excess cyanide must be used or vice versa.

Rinse Waters. A proprietary in-line, integrated system of chrome reduction employing the same physical arrangement as shown on Figure 2 has been proposed by Lancy. It employs chemical treatment with sodium hydrosulfite at neutral pH to reduce chromates. The trivalent chromium formed precipitates as the hydroxide and is separated in the chemical tank. From the chemical tank, the sludge is bled to the acid-alkaline waste treatment system.

A novel method of chromate reduction involves reduction with scrap iron by the cementation process. Under low pH conditions, chromate

$$CrO_4^{=} + Fe^{\circ} = 8H^{+} \longrightarrow Cr^{+++} + Fe^{+++} + 4H_2O$$

is reduced to chromic ion and iron goes into solution as ferric iron. Some iron also goes into solution as ferrous ion by reaction with hydrogen ion. Thus, the

$$Fe^{\circ} + 2H^{+} \longrightarrow Fe^{++} + H_2$$

metal ion content of the wastewater is doubled, at least.

The cementation process is especially valuable when copper bearing wastes are present, because

$$Fe^{\circ} + Cu^{++} \;\underline{\qquad\qquad}\; Cu^{\circ} + Fe^{++}$$

copper ion is reduced to metallic copper, which can be recovered. In situations where both chromates and copper ions are present, the cementation process serves to reduce chromates effectively and provides for recovery of a large part of the copper.

The conventional system of chromate reduction employs the use of sulfur dioxide or sulfites. In some locations, it is advantageous to use flue or stack gas to supply the sulfur dioxide. Such an operation serves to remove an important air pollutant from flue gas and could make use of a high sulfur fuel a feasible matter.

Batch versus Continuous Flow Treatment

Batch type systems provide the highest degree of reliability possible in terms of effluent quality. Some states now require that all chromate and cyanide wastes be treated on a batch basis. With the growing concern for fail safe operation and stricter effluent standards, it seems certain that batch treatment will be favored in all but the largest plants where skilled maintenance personnel are available to maintain performance of automated, continuous flow systems.

Chemical Recovery

Plating Baths. The opportunities for increasing chemical recovery from cyanide baths are almost nil. Efforts to reduce solids "carry-in" into the plating bath by use of demineralized water for a final rinse in advance of plating serve to prolong the usefulness of plating baths and, therefore, serve the same purpose. Some platers claim they never dispose of cyanide baths.

Chromic acid can be reclaimed from both spent baths and rinse waters by use of anion exchange. The life of chromic acid baths can be prolonged by use of external cation exchange units.

Rinse Waters. Chromates can be reclaimed by use of anion exchange units.

Solids Handling

Disposal of the metal hydroxide sludges generated in treatment of plating wastes has been a difficult problem because of their gelatinous nature. Filtration is normally very difficult.

Recent studies, primarily in conjunction with the cementation process have demonstrated that a two-stage system of neutralization, employing sludge recirculation, will produce sludges that are readily dewaterable by vacuum or pressure filtration. Additional studies have demonstrated that marked improvement in the filterability of all sludges can be made by using two-stage neutralization.

GENERAL PLANNING CONSIDERATIONS

This chapter discusses the effects that the metal plating industry is expected to exert on water resources. Anticipated changes to the present practices within this industry are expected to occur largely as a result of the actions of enforcement authorities requiring improvements in water pollution control.

Water Supply

The greatest use of water is for rinsing of products The purpose is to remove drag-out chemicals from each process bath and prevent their being transferred as impurities to the next bath. The amount of water used depends to a great degree upon management practices at the plant. The plating process does not have to be a large water user and should not be considered such in water resources planning. The majority of plants use under 0.1 mgd of water. In the Merrimack River basin there are only four plants known to use in excess of this amount.

Various water conservation practices are being implemented by metal plating industries that have a marked effect on water use. Counterflow rinsing practices can decrease water use to 25 percent of flow through. Use of ion exchange equipment permits nearly complete recirculation of rinse water.

Industrial water quality requirements are such that, if available, plants usually use public water supplies for rinse water. Although potable water is not needed from a bacteriological point of view, a supply low in mineral content is highly desirable. Waters high in total dissolved solids are acceptable for use following demineralization. Direct use results in excessive drag-in of impurities to baths requiring frequent regeneration or disposal. Brackish water is not an acceptable supply for this industry.

Effluent Discharge

The conventional methods of treating metal plating wastes are capable of producing an effluent of satisfactory quality for discharge into a water body designated for any use. Pollution attributed to this industry is usually caused by accidental discharges or poor housekeeping practices. Since metal plating wastes are extremely toxic, reliable controls are necessary.

Use of the batch treatment method provides a reliable means of waste quality control because each batch can be tested to confirm the adequacy of the treatment prior to its release to the receiving waters.

In the case of continuous treatment, reliability is considerably diminished despite the use of automatic monitors to control the quality of effluent. Some state codes do not permit continuous treatment of metal plating wastes prior to discharge to streams.

Solids Handling

The biggest problem in waste disposal from metal plating involves the handling of solids. Precipitated metal hydroxides have a specific gravity close to unity, making the settling and densifying of the sludge difficult.

The sludge is mainly composed of hydroxides of metals used in each particular plating process. After thickening, the sludge is normally about five to ten percent by volume of the total wastewater flow. Vacuum filtration further reduces the volume to between a half and one percent of the total flow.

Final disposal of sludge should be by stockpiling with a view to future materials recovery and reuse when technology makes such efforts feasible. Stockpiles should be covered to eliminate the possibility of sludge being washed into nearby streams.

Stockpiling is a safe procedure as long as the sludge is not exposed to acidic conditions. An acidic environment would permit the metal hydroxides to go back into solution. For this reason, metal plating wastes should not be dumped together with organic wastes at sanitary landfill sites where acid fermentation of the organic wastes may cause the hydroxides to go into solution.

Cost Considerations

Generalization of treatment costs for the metal plating industry provides no more than broad order-of-magnitude values because variables affecting these costs are numerous. Table 7, which has been reproduced from Ref. 9, provides an example of this point by showing variations in treatment costs with work shifts.

Similarly, a major impact on the cost of treatment is the shape of the material plated. Table 8, reproduced from Ref. 4, shows variations in dragout rate with the type of material plated. Dragout is the amount of plating material which becomes a source of pollution in the rinse water.

A survey of published cost data, supplemented with data from our files, provides some guidance on plating wastes treatment costs for use in water resource planning in the Merrimack River basin. Construction and annual operation costs were collected separately for plants providing treatment to concentrated wastes and rinse waters, and for plants treating rinse waters only. The costs were generally confined to those using conventional treatment methods. Figure 3 shows these data plotted against average daily volume of waste treated. Costs shown represent present day prices.

Table 7. Alternatives Considered in Wastes Treatment Plant Design

Scheme	Cyanide Oxidation	Skimming and Precipitation	Operating Time (hr./day)	Ultimate Capacity (mgd)	Costs[1] ($) Capital	Costs[1] ($) Annual Operating
1	Batch	Batch	24	0.48	40,000	2,700
2	Batch	Batch	16	0.48	56,000	6,700
3a	Continuous	Continuous	8	0.96	26,000	8,000
3b	Continuous	Continuous	16	0.48	6,000	4,000
3c	Continuous	Continuous	24	0.32	0	0
4a	Batch	Continuous	8	0.96	40,000	8,000
4b	Batch	Continuous	16	0.48	15,000	4,000
4c	Batch	Continuous	24	0.32	9,000	0

[1] Referred to Scheme 3c as basis.

Table 8. Variation in Dragout Rate with the Type of Material Plated

Type of Material	Dragout Rate
Vertical, well drained	0.4-1.0 gal/1000 ft^2
Vertical, poor drainage	2-3 gal/1000 ft^2
Vertical, very poor drainage	4-5 gal/1000 ft^2
Horizontal, well drained	0.8-2.0 gal/1000 ft^2
Horizontal, very poor drainage	10 gal/1000 ft^2
Cup shaped work, very poor drainage	24 gal/1000 ft^2
Barrel - angle	2-9 fluid ounces per load
Barrel - horizontal	5-30 fluid ounces per load

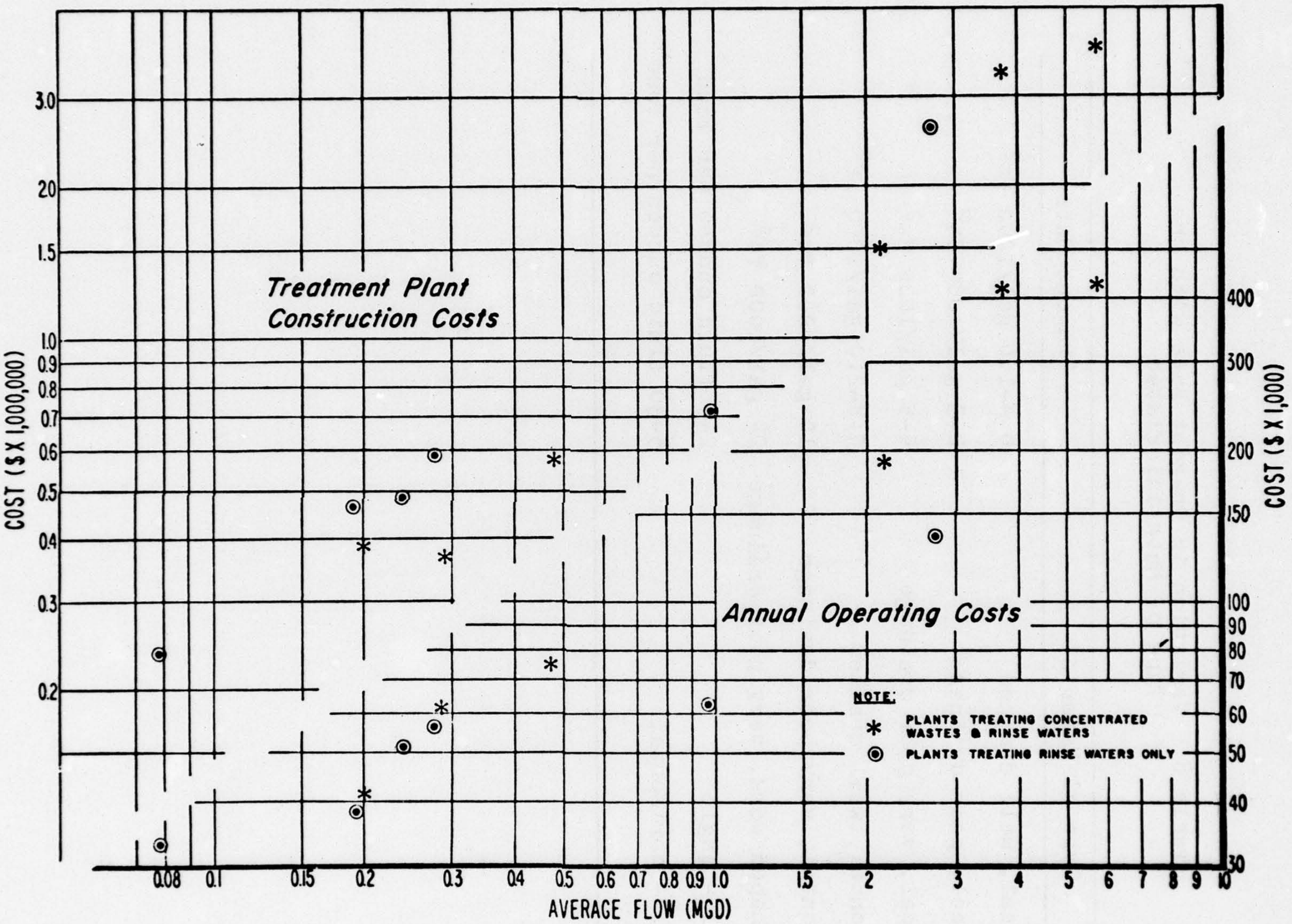

Fig. 3

CONVENTIONAL PLATING WASTE TREATMENT COST DATA

Future Impact of Plating Wastes on Water Resources

As mentioned earlier in the report, the most compelling reason for changes in plating waste disposal procedures is the application of higher standards in water pollution control. Product reuse is expected to remain generally as a secondary benefit.

Table 9 shows the type and value of products that may be recovered from plating rinse waters.(9)

Table 9. By-Product Recovery in Plating and Allied Industries

		By-Product Recovery		
Process	By-Product	Concentration Range (mg/L)	Value ($/1000 gal.)	Diminution of Pollutional Load
Rinse waters	Nickel	150-900	0.80-7.00	80-100%
	Copper	2-20	0.01-0.10	80-100%
		100-500	0.60-3.00	80-100%
	Zinc	70-350	0.40-2.40	80-100%
	Silver	50-250	1.60-9.00	80-100%
	Chromium	400-2000	3.20-15.00	80-100%
	Cadmium	50-250	1.20-6.00	80-100%
	Brass	(Cu) 40-250	0.20-1.20	80-100%
		(Zn) 10-60	0.20-1.20	80-100%
	Tin	100-600	0.80-4.80	80-100%
	Gold			
	Platinum			

The value of water reuse can be measured by the price of water paid to municipalities. In Massachusetts, municipalities typically charge $200 to $400 per million gallons.

It is expected that treatment of cyanide bearing wastes will continue to be by oxidation with chlorine to the complete destruction of cyanide in batch operations. In the continuous treatment operation, if permitted by enforcement agencies, the same process is expected. However, safeguards to insure high quality are expected to be required.

For chrome bearing wastes, the cementation process is predicted to become the favored method because of its simplicity and because hexavalent chrome can be reduced to negligible quantities.

The removal of trivalent chrome and heavy metals is expected to be carried out by precipitation at a pH range of 8.5 to 9 with lime. In batch operations no additional clarification of the effluent is anticipated. However, where continuous flow treatment is practiced, *filtration of the* effluent should be expected. When copper is present in the waste in significant amounts, the cementation process is likely to be employed for partial recovery of this metal.

Solid waste disposal is expected to remain a problem. Any product recovery process presently employs a process of substitution which does not tend to decrease the volume of solids significantly. For example, the cementation process substitutes iron to recover copper. Ion exchange regenerates metals, but uses excess chemicals to accomplish this. Volatilization is not a process applicable to this waste.

In general, a marked decrease in the discharge of liquid effluent is expected, but solid waste is not expected to decrease.

In all new plants and in many existing ones, it is predicted that two-stage neutralization of wastewaters will be practiced. Although this will not decrease the dry weight of solids requiring disposal, it will materially reduce the volume and manageability of the sludge under stockpiling practices.

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THE NATURE AND TREATMENT
OF
TEXTILE EFFLUENT

Prepared for
U. S. Army Corps of Engineers

by
THORSTENSEN LABORATORY
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COMMONWEALTH OF MASSACHUSETTS
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July 15, 1971

THE NATURE AND TREATMENT OF TEXTILE EFFLUENT

TABLE OF CONTENTS

This report is a survey of the waste problems of the textile industry. The information reported here is based, to some extent on the industry profile report of the Water Quality Office. That report was supplemented by specific reference investigation and the writer's experience in the industry.

This report will be in several sections with the first being a review of the causes of pollution in the textile industry and then we will relate this to specific types of cloth and textile plants. The effluent produced in the various types of plants will be identified under each section and the methods of processing will be discussed together with references to the various types of textiles being produced. Within the limitations of time and space, we will attempt to emphasize the possibilities of future treatment of textile wastes.

TEXTILE WASTES GENERAL INFORMATION

There are only 2 sources of pollution that are common in the textile industry. One of these sources is associated with the fiber itself such as natural impurities which will be extracted from the fiber and the other source is the chemicals used in processing of the fibers. Cotton and wool are natural fibers that contain substances which are extracted from the fibers during processing. In working with synthetics, certain materials may be extracted during processing, but their contribution to the pollution load is so small that it can be considered negligible. Among the processing chemicals which contribute to the pollution load are those materials that have been added to the fiber in earlier processing that must be removed in subsequent operations. These include materials like sizing, spinning lubricants, anti-static oils, etc. The processing chemicals also contribute to the pollution load because they are not fixed to the fiber. These include spent dyes, detergents and related products. In considering the pollution loads of this industry, we will limit the discussion to those materials that are contributors to the aqueous pollution load.

COTTON AND COTTON BLENDS

In the Water Quality Office Report, a flow sheet is given for the processes used in the cotton industry. Although several types of cotton are indicated, for the purposes of this report we will concentrate on a single line of cotton woven fabrics.

Individual textile mills may have great versatility and processes may change considerably for the season of the year and the fashions of the time. The operation in the cotton mill can be simplified to processes such as carding and combing, slashing, weaving and other mechanical operations. In these initial operations, the trash and foreign matter are mechanically removed from the raw cotton, the fibers are straightened, drawn into thread, and wound on spools. The thread is then run through starch solutions (slashing) so that it has the strength and stiffness to withstand the friction generated in the weaving

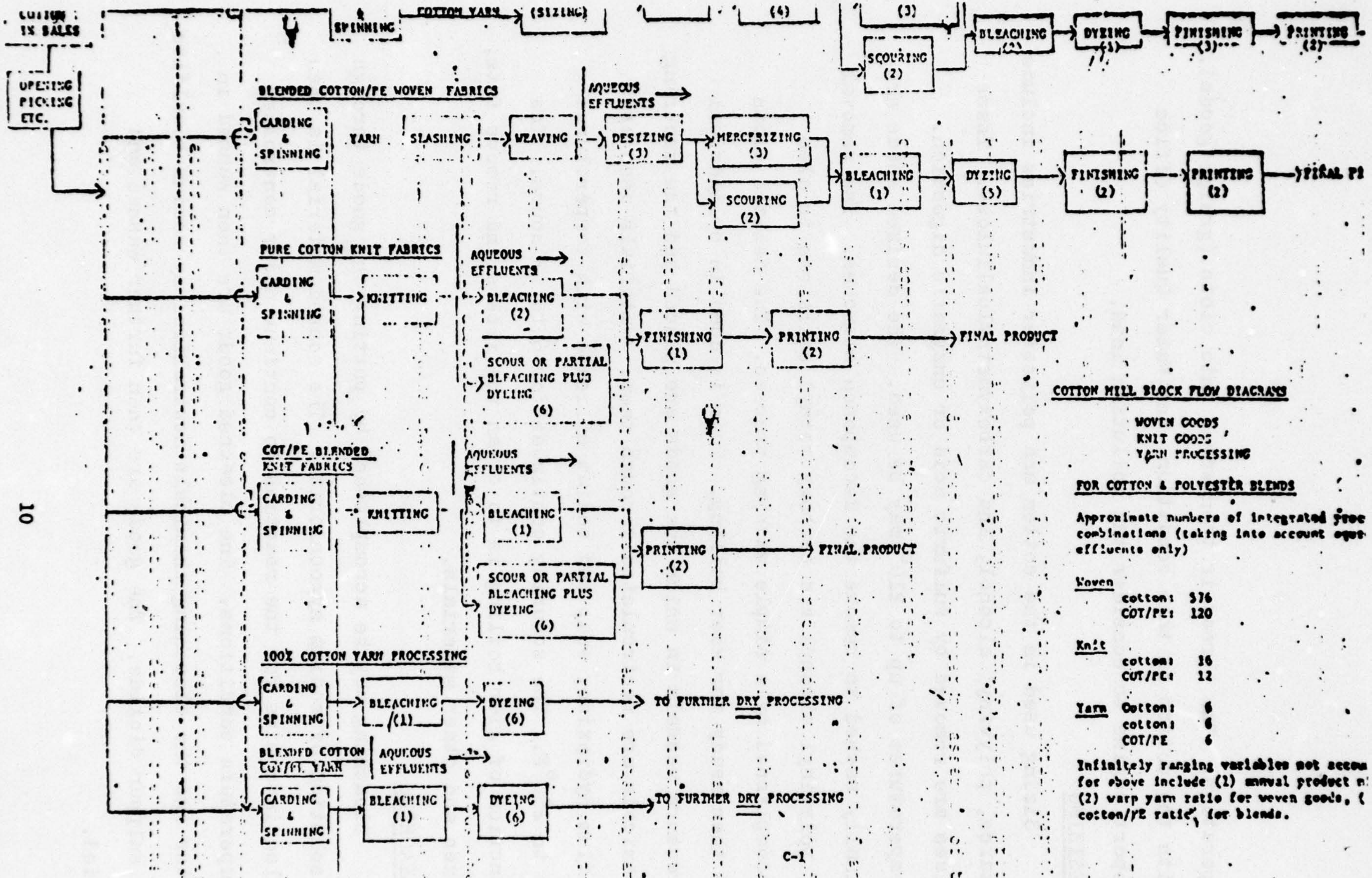

COTTON IN BALES
OPENING PICKING ETC.
SPINNING
COTTON YARN
(SIZING)
(4)
(3)
SCOURING (2)
BLEACHING (2)
DYEING (4)
FINISHING (3)
PRINTING (2)
BLENDED COTTON/PE WOVEN FABRICS
AQUEOUS EFFLUENTS
CARDING & SPINNING
YARN
SLASHING
WEAVING
DESIZING (3)
MERCERIZING (3)
SCOURING (2)
BLEACHING (1)
DYEING (5)
FINISHING (2)
PRINTING (2)
FINAL PE
PURE COTTON KNIT FABRICS
AQUEOUS EFFLUENTS
CARDING & SPINNING
KNITTING
BLEACHING (2)
SCOUR OR PARTIAL BLEACHING PLUS DYEING (6)
FINISHING (1)
PRINTING (2)
FINAL PRODUCT
COT/PE BLENDED KNIT FABRICS
AQUEOUS EFFLUENTS
CARDING & SPINNING
KNITTING
BLEACHING (1)
SCOUR OR PARTIAL BLEACHING PLUS DYEING (6)
PRINTING (2)
FINAL PRODUCT
100% COTTON YARN PROCESSING
CARDING & SPINNING
BLEACHING (1)
DYEING (6)
TO FURTHER DRY PROCESSING
BLENDED COTTON COT/PE YARN
AQUEOUS EFFLUENTS
CARDING & SPINNING
BLEACHING (1)
DYEING (6)
TO FURTHER DRY PROCESSING
COTTON MILL BLOCK FLOW DIAGRAMS
WOVEN GOODS
KNIT GOODS
YARN PROCESSING
FOR COTTON & POLYESTER BLENDS
Approximate numbers of integrated proc
combinations (taking into account aque
effluents only)
Woven
cotton: 576
COT/PE: 120
Knit
cotton: 36
COT/PE: 12
Yarn
Cotton: 6
cotton: 6
COT/PE 6
Infinitely ranging variables not accou
for above include (1) annual product m
(2) warp yarn ratio for woven goods, (
cotton/PE ratio for blends.
C-1

FIGURE 1

operation. The thread is then woven into cloth (greige goods). With the cotton in this condition, the Water Quality Office Report begins to consider the pollution load.

DESIZING

Sizing used in the cotton and polyester industries include starch, polyvinyl alcohol, and carboxymethylcellulose. These sizes are removed by sulfuric acid or enzymatic digestion. Temperatures of up to 210° may be used. The desized goods are finally washed to remove the decomposed starches. The removal of polyvinyl alcohol and carboxy methyl cellulose is also accomplished by a simple washing process. The desized cloth is then ready for kier boiling. This is done in cylindrical pressure vessels in which the goods are placed and the scouring chemicals are recirculated through them. Materials used are sodium hydroxide, soap and sodium silicate with temperatures up to 250°F. The scouring continues for 6 to 12 hours. The function of kier boiling is to clean the fibers and remove fats, waxes and other materials.

BLEACHING

Bleaching may be accomplished by putting the goods through a solution of sodium hypochlorite. The soaked material is then piled into bins for the reaction to continue under controlled temperature conditions. The bleached goods are then washed in water and the bleaching chemicals neutralized by sodium bisulfite or sulphur dioxide. The goods are then further washed and dried.

MERCERIZATION

Mercerization is an important step in cotton manufacture for preparation of the fibers for dyeing, printing and finishing. The exact mechanism of the process is not fully understood, but in the process, the goods are immersed in strong solutions of sodium hydroxide for extended periods of time. This results in increased tensile strength, lustre, reduction of potential shrinkage and increases the affinity of dyes. There is some swelling of the fibers, the degree of which will depend on the time, temperature and concentration of the materials used. The effluent from this process is strong sodium hydroxide. Mercerization is generally a continuous process with the goods in contact with the solutions for 1 to 3 minutes. The cloth is rinsed in water and given an acid dip followed by a water wash prior to dyeing.

DYEING

For dyeing of cotton, several different types of dye are used.

Direct dyes can be applied directly to the cloth. These are usually low cost, easy to apply but they "take" rather slowly.

Developed dye is applied to the cloth and is developed by the addition of a secondary chemical called a developer. These dyes generally have good wash-fastness.

In sulphur dyeing, the dye is put on the cloth in a reduced state and oxidized to produce the color. Dichromate or peroxide may be used as the oxidizing agents, although air may be used.

Dispersed dyes are applied to the fabrics not as solutions but as suspensions. First used on the synthetic fibers, they dye by absorption into the fibers.

Vat dyes are applied to fibers in a reduced state and then oxidized on the fiber. Vat dyes are not soluble in water but are given water solubility and fiber affinity by the use of sodium hydroxide and sodium hydrosulfite.

Napthole dyes are applied to the fabric and passed through a developer, then diazotation takes place after the naphol has been applied to the fiber.

Fiber reactive dyeing bonds the fiber to the dyestuff established by chemical reaction rather than simple absorption. In this process, the dyes are usually padded on to the cloth and allowed to remain in a saturated condition for a day or more to complete the reaction.

In any of the dyeing operations, the chemicals will consist of unfixed dyes and reactive assistant materials. They may be refractive to biodegradability printing.

PRINTING

In printing the concentration of the dye is considerably higher than in the batch processes. The application of color and pattern may be done by printing press, the roller print machine or a screen print machine.

After the printing, the goods are steamed or aged, or otherwise treated to fix the dye. A major source of pollution load in textile manufacturing is the washing of printing equipment, and the washing of the cloth to free it from the unfixed dyes. The same general types of dyes are used for printing as are used in dyeing.

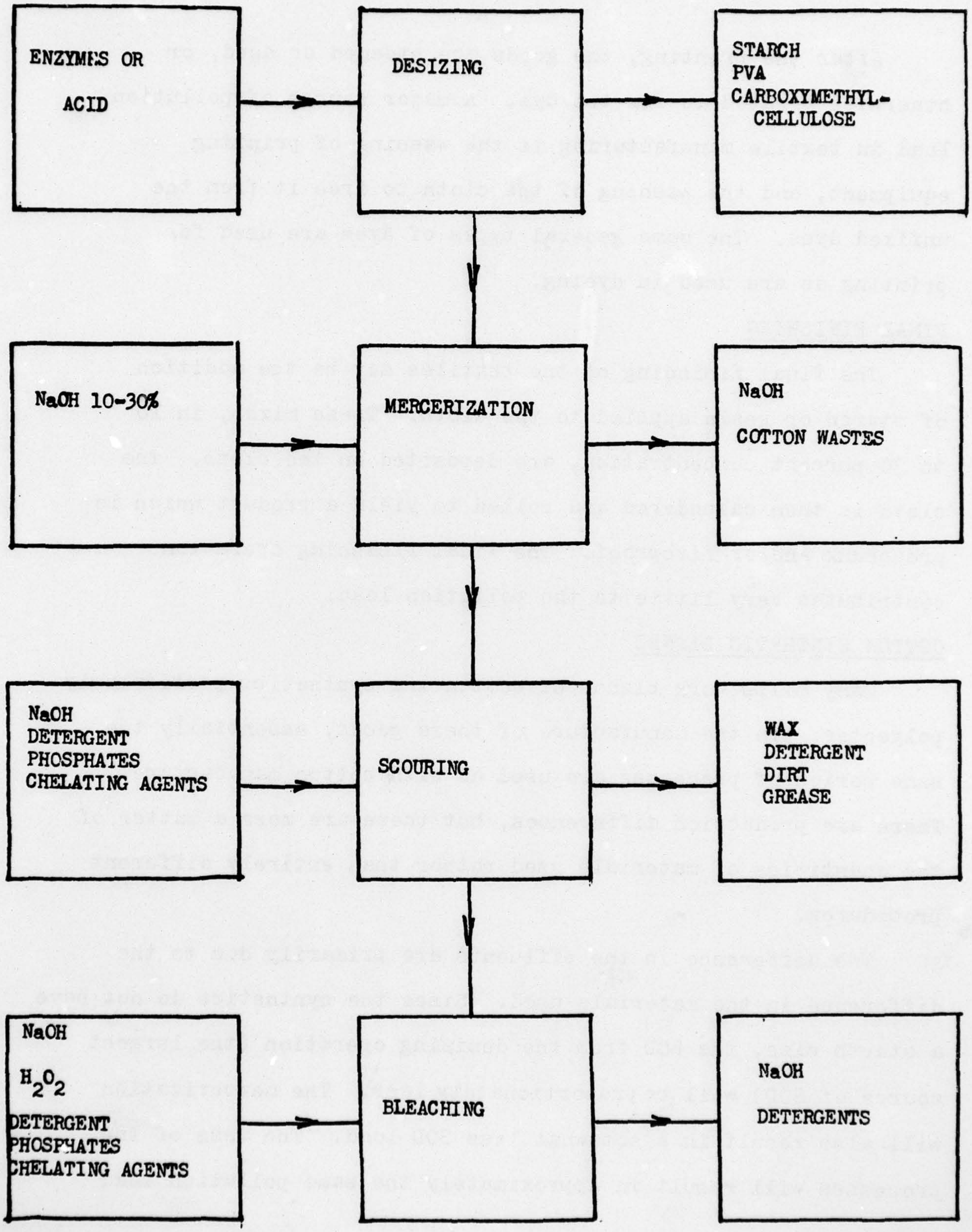
FINAL FINISHING

The final finishing of the textiles may be the addition of starch or resin applied to the cloth. These mixes, in 10 to 30 percent concentration, are deposited on the cloth. The cloth is then calendered and rolled to yield a product which is preshrunk and/or fireproof. The final finishing operation contributes very little to the pollution load.

COTTON SYNTHETIC BLENDS

Many mills work blends of cotton and synthetics particularly polyester. In the manufacture of these goods, essentially the same series of processes are used as with cotton manufacture. There are production differences, but these are more a matter of the quantities of materials used rather than entirely different procedures.

The difference in the effluents are primarily due to the difference in the materials used. Since the synthetics do not have a starch size, the BOD from the desizing operation (the largest source of BOD) will be proportionately less. The mercerization will also result in a somewhat less BOD load. The rest of the processes will result in approximately the same pollution load


ENZYMES OR
ACID
DESIZING
STARCH
PVA
CARBOXYMETHYL-CELLULOSE
NaOH 10-30%
MERCERIZATION
NaOH
COTTON WASTES
NaOH
DETERGENT
PHOSPHATES
CHELATING AGENTS
SCOURING
WAX
DETERGENT
DIRT
GREASE
NaOH
H2O2
DETERGENT
PHOSPHATES
CHELATING AGENTS
BLEACHING
NaOH
DETERGENTS

COTTON

PROCESS	WASTE CHARACTERISTICS at:	lbs/1000lbs
Desizing:	Starch Sizing:	PVA:
BOD	45	3-4
Suspended Solids	89	5
Dissolved Solids	6	45
pH	6-8 enzyme 1-2 Acid	6-8
Oil & Grease	5	3-10
Effluent Water	1500 gal.	1500 gal.

*****

Mercerization:	
BOD	2 - 12
Suspended Solids	5
Dissolved Solids	146
pH	12 (.8% NaOH)
Color	--
Oil & Grease	10
Effluent Water	2,000 gal.

*****

Scouring:	
BOD	16-20 lbs
Suspended Solids	5
Dissolved Solids	50
pH	12.5 (.25% NaOH)
Color	--
Oil & Grease	30-40
Effluent Water	3,000 gal.
P	1

COTTON, continued

PROCESS	WASTE CHARACTERISTICS at: lbs/1000 lbs.
Bleaching:	
BOD	1
Suspended Solids	4
Dissolved Solids	20-50
pH	11
Color	--
Oil & Grease	--
Effluent Water	2,000 gal.

*****

PROCESS	WASTE CHARACTERISTICS at: lbs/1000 lbs.
Dyeing:	
BOD	3-20
Suspended Solids	--
Dissolved Solids	50-200
pH	1-2, 6-8, 12
Color	1-3
Oil & Grease	--
Effluent Water	5,000 gal.

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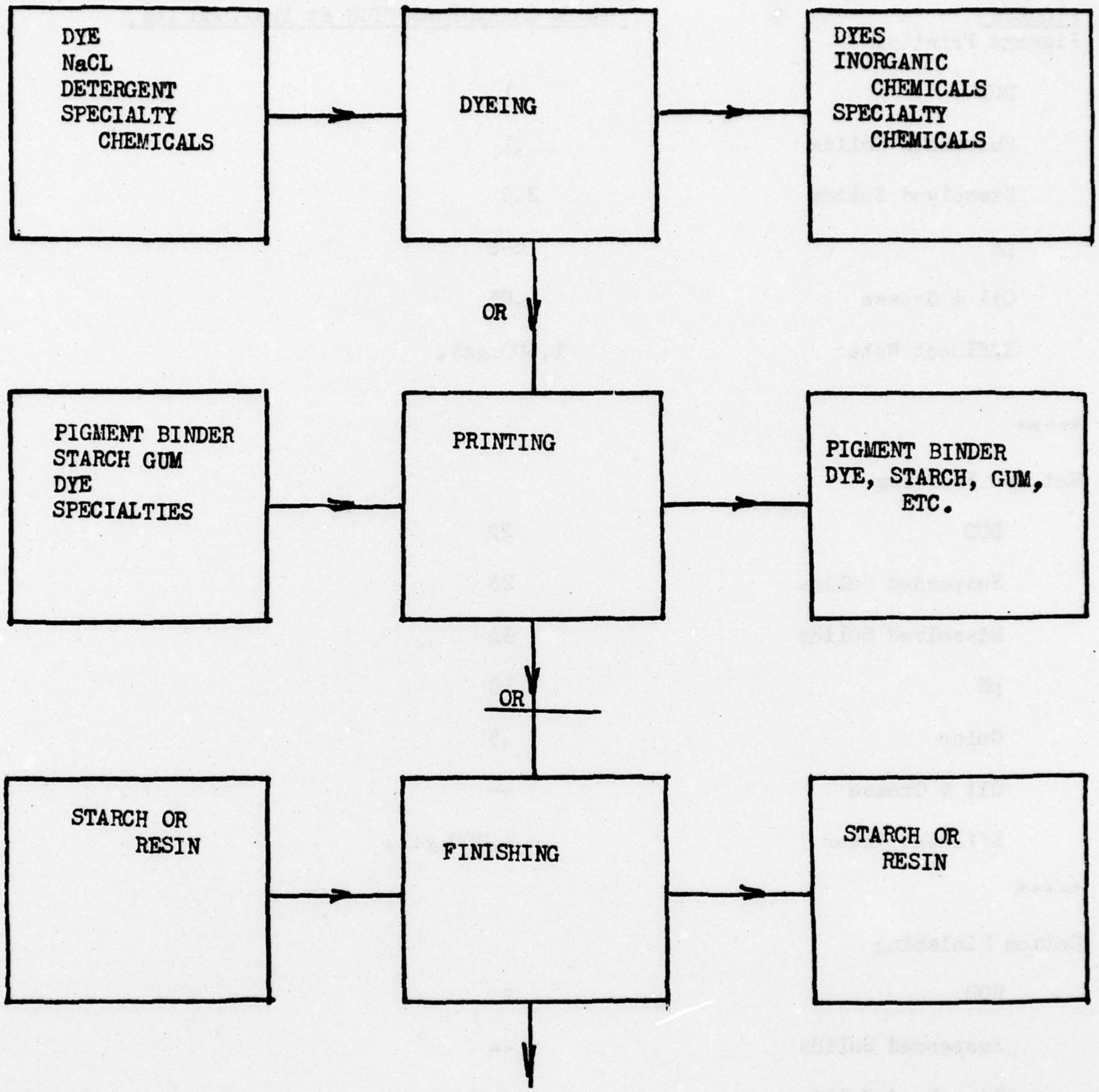

DYE
NaCL
DETERGENT
SPECIALTY
CHEMICALS
DYEING
DYES
INORGANIC
CHEMICALS
SPECIALTY
CHEMICALS
OR
PIGMENT BINDER
STARCH GUM
DYE
SPECIALTIES
PRINTING
PIGMENT BINDER
DYE, STARCH, GUM,
ETC.
OR
STARCH OR
RESIN
FINISHING
STARCH OR
RESIN

COTTON

PRINTING

PROCESS	WASTE CHARACTERISTICS at lbs/1000 lbs.
Pigment Printing	
BOD	1
Suspended Solids	.1
Dissolved Solids	2.5
pH	6-8
Oil & Grease	.05
Effluent Water	1,500 gal.
*****	
Vat Dye Printing	
BOD	22
Suspended Solids	25
Dissolved Solids	34
pH	10
Color	.5
Oil & Grease	--
Effluent Water	4,000 gal.
*****	
Cotton Finishing	
BOD	2
Suspended Solids	--
Dissolved Solids	5-22
pH	6-8
Color	--
Oil & Grease	--
Effluent Water	1,500 gal.

Following are the combined wastes of the above:

COMBINED WASTES, total of cotton Processes

BOD	141
Suspended Solids	129
Dissolved Solids	300
pH	--
Color	--
Oil & Grease	50
Effluent Water	17,500 gal. plus washes

*****

from detergents, dyes, inorganic materials, and specialty chemicals as is found in cotton production.

WOOL

The manufacture of wool is divided into 2 sections by normal industrial practice. These are wool top making and wool blends finishing. This is based partly on the differences in the manufacturing process and partly because the wool is usually partially treated by one plant and completed by another. The wool processing is a specialized industry and operations may be only one phase of the industry. Wool top making is a process of converting greasy wool as received from the sheep farmers into clean wool called top for the use in the manufacture of fabrics and felts. Wool blends finishing refers to all of the operations in the processing of the clean wool into the final cloth. This may include knitting mills, weaving mills, worsted mills and others.

DESUINTING

When wool is received at the scouring plant it contains a large quantity of waste materials called suint. This suint includes dirt, secretions of the sheep, urine, feces, sweat, and blood. The dirt is vegetable fibers, oily matter, soil and wool grease. For every pound of purified or scoured wool that is made there are about ½ lbs of impurities removed from it. Much of this is discharged into waste. The wool is desuinted by washing with fresh water from which the heavy solids settle.

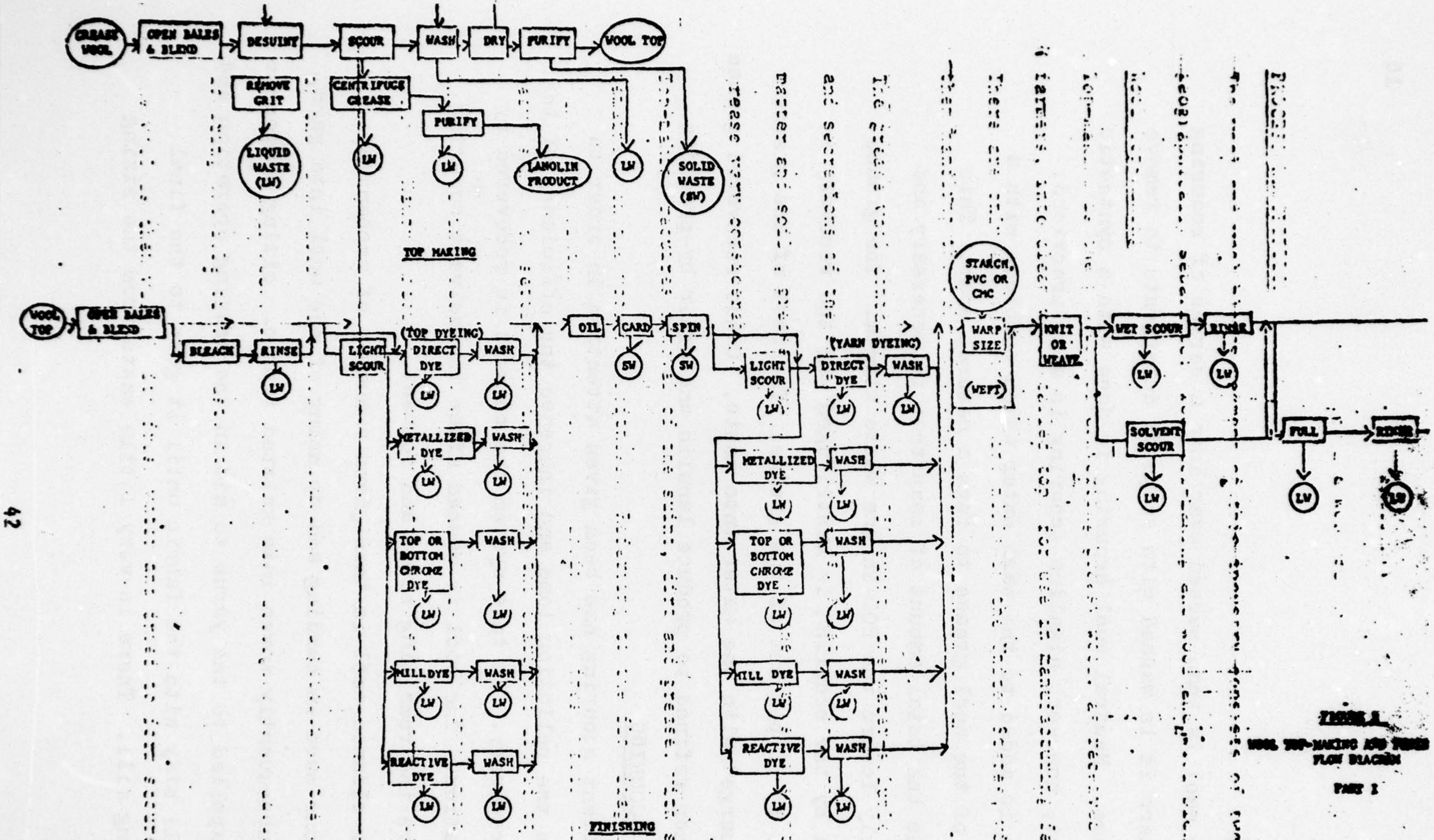


FIGURE 1.

WOOL TOP-MAKING AND [illegible]
FLOW DIAGRAM

PART I

SCOURING

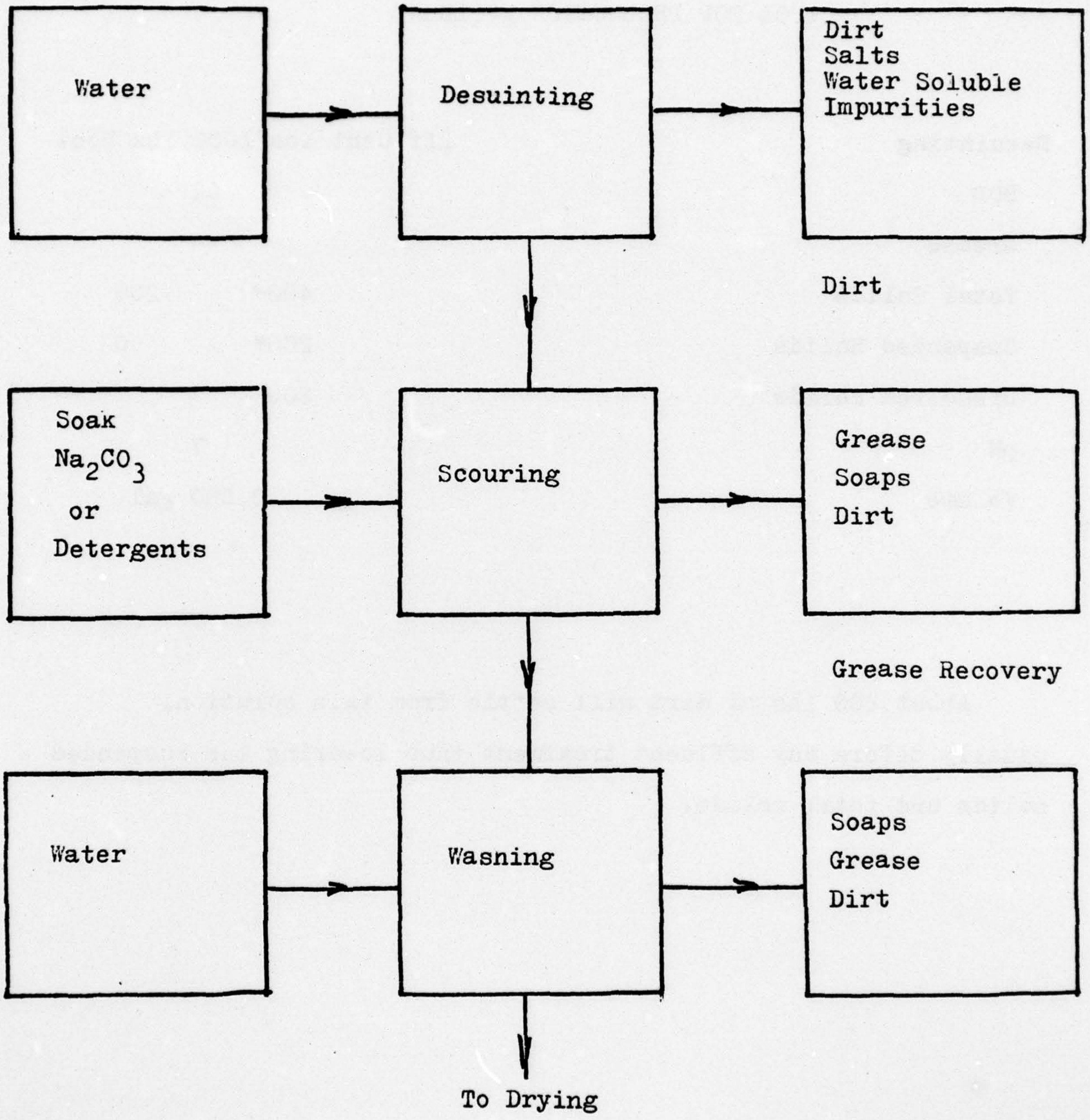
The wool is then passed over into a series of scouring bowls where it is washed with soaps or detergents to remove the grease. Neutral wool scouring is done with a synthetic detergent, however, alkaline scouring is also practiced. Soda ash is added to the wash water which combines with a portion of the wool grease to form a natural soap. This decreases the total amount of soap that is necessary and apparently lowers the BOD in the waste stream. The grease produced by the scouring is centrifuged and the recovery is about 25 to 50 percent of the grease. The rest of the grease is discharged with the water into waste. Crude recovered grease is further refined to produce lanolin and other by-products.

SOLVENT SCOURING

Solvent scouring has been given attention in order to decrease the pollution load and increase the efficiency of the grease recovery. In this system the solvent is recovered by distillation. The wool is washed after the solvent scouring to remove the remaining suint and solvent.

The cleaned wool is then given a number of mechanical operations such as carding and spinning of the wool into yarn. It is subsequently woven into knitted fabric. sizing compounds may be applied to the yarns to aid in the weaving operation and they will stay with the fabric until it goes to the final finishing mill. There is very little waste from the sizing baths.

WOOL TOP PRODUCTION



WOOL TOP PRODUCTION EFFLUENT

Desuinting	Effluent lbs/1000 lbs Wool	
BOD	60	
Grease	--	
Total Solids	400*	200
Suspended Solids	200*	0
Dissolved Solids	200	
pH	7	
Volume	2,650 gal	

About 200 lbs of dirt will settle from this solution, usually before any effluent treatment thus lowering the suspended solids and total solids.

WOOL TOP PRODUCTION

Scouring

	lbs/1000 lbs Wool	
	Before Grease Removal	After Grease Removal
BOD	230	230
Grease	165	100
Total Solids	284	254
Suspended Solids	145	145
Dissolved Solids	64	34
Detergent	30	30
pH	8	8
Volume	680	2050

WOOL TOP PRODUCTION

Washing	lbs/1000 lbs Wool
BOD	10
Grease	--
Total Solids	51
Suspended Solids	23
Dissolved Solids	28
pH	8
Volume	5300

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THE MERRIMACK: DESIGNS FOR A CLEAN RIVER. CONSULTANT'S INDUSTRI--ETC(U)
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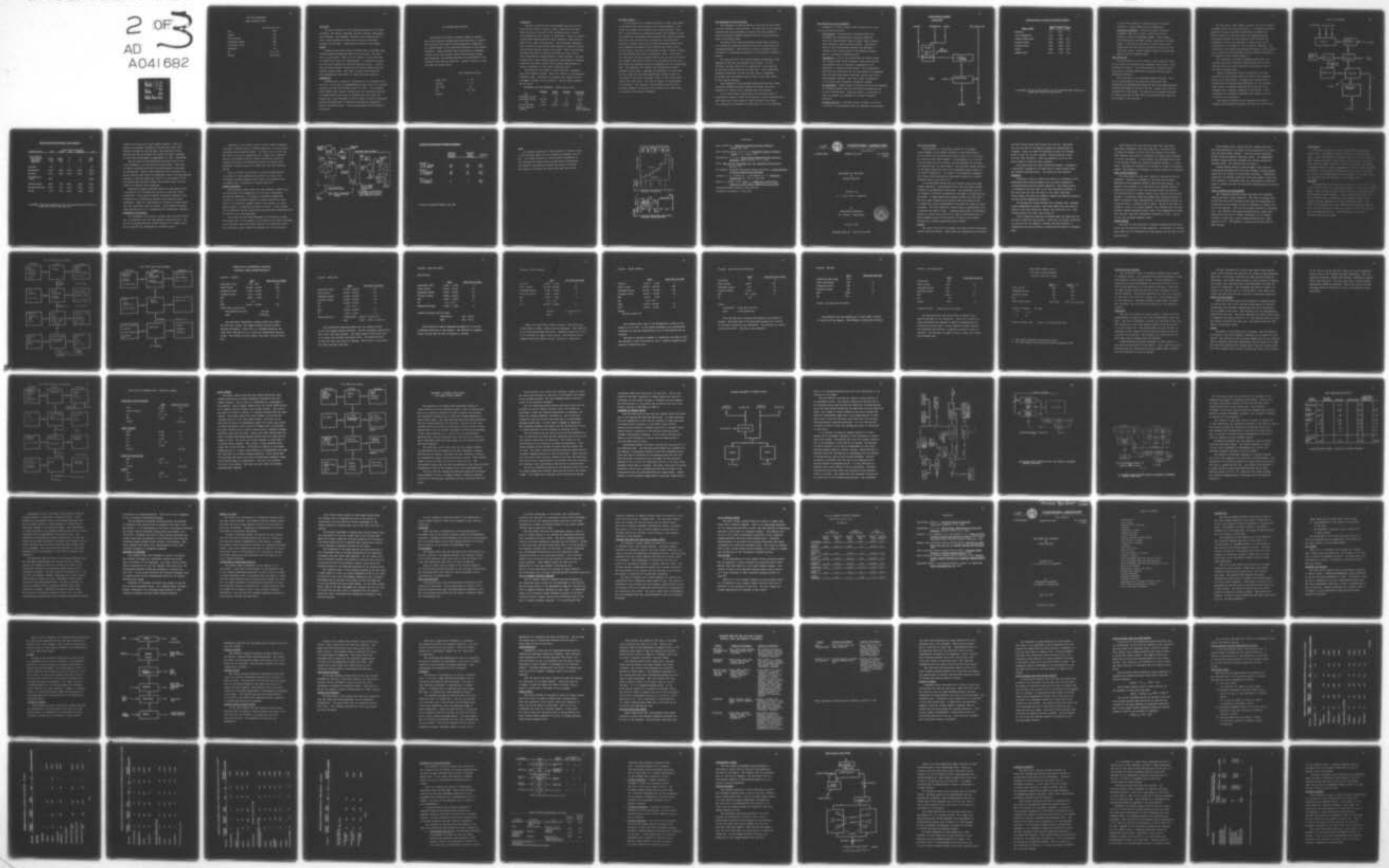

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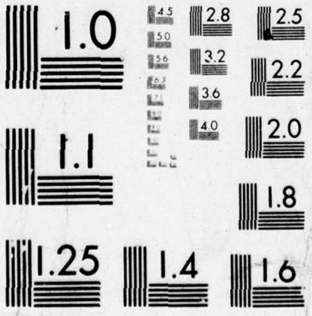


MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

WOOL TOP PRODUCTION

TOTAL POLLUTION LOAD

	lbs/1000 lbs Wool
BOD	300
Grease	100
Total Solids	505
Suspended Solids	168
Dissolved Solids	337
Detergent	30
pH	7.5 - 8.5
Volume	10,000 gal

FINISHING

The major processes in the finishing operation in the wet processes, are dyeing, scouring, fulling, washing, carbonizing and bleaching. The original scouring at the finishing mill is only a light scouring to remove any sizing and finishing materials on the wool. Following this there is the dyeing.

DYEING

Dyeing of wool can be done in either open or pressure type vessels using acid dyes and salts to fix the dye. The dyed wool is then fulled. This is a wet process in which the wool is treated with soap as a felting agent. By mechanical action, the wool then tightens on itself and becomes firmer. Worsted wool and most synthetic blends are not fulled because they are already tightly woven. The fabric is dyed either before or after fulling and then washed to remove process chemicals.

CARBONIZING

Carbonizing is a means of removing non wool substances from the wool. It is done by impregnating the wool with 4 to 6 percent sulfuric acid and oven drying at 212° to 220°F. The treatment with sulfuric acid causes a breakdown of the cellulosic material as charred matter which can be separated from the fabric by flowing air. The finishing of woolen blends is done by mechanical methods including ways of steaming, pressing and shearing to obtain a uniform surface. Moth proofing agents may be added at this point.

WOOL DYEING AND FINISHING

Scoured and dried wool is usually combed in another plant and processed through dyeing and finishing in another. The pollution load (BOD) of these processes is dependent, to a great extent, on the type and efficiency of the dyeing operation. These processes give essentially no suspended solids, but do have soluble solids from desizing, dyeing and finishing. The fulling operation can contribute to the pollution load from the soap used. Typical values for these processes are given below:

	BOD lbs/1000 lbs Wool
Light Scour	0 - 50
Fulling	0 - 16
Pre Scour	20
Dye	15 - 226
Finish	0

SYNTHETICS

Synthetic materials are the man-mades and include such materials as acetate, acrylic, nylon, polyesters and rayon. These fibers, as received at the finishing plant, require no processing for the removal of impurities. They do, however, contain some sizings and anti-static materials which must be removed by a light scouring bath. The anti-static materials are a problem as they include such things as polyvinyl alcohol styrene based resins, glycols and others. After the scouring, the goods are dyed or bleached followed by a rinse and a final finishing for waterproofing or other finishes. The BOD loading total solids figures given are representative averages taken from the Water Quality Office report supplemented by current literature on the textile effluent field.

The dyeing of the fibers is quite different depending upon their chemical nature. This will reflect in the auxiliary chemicals used. Polyester, for example, may require the use of organic solvents as dye carriers. Some of these solvents may be toxic.

POLLUTION LOAD FOR SYNTHETICS TOTAL lbs/1000 lbs

	Acrylic	Nylon	Acetate	Polyester
BOD	5	5-24	6	100-200
Suspended Solids	--	----	--	-----
Dissolved Solids	110-140	60	10	80-90
pH	6-8	7-9	6-7	6-8
Volume Gallons	10,000	14,000	10,000	35,000
Toxic Materials Present	--		--	Phenols & Chloro Benzene

NONWOVEN FABRICS

In the production of nonwoven fabrics or felts, any number of man-made fibers may be used as the fibrous material. The fibers are combed, and airborne into a loose felt mat. This mat is then dipped by a continuous process into synthetic resin bath emulsions containing acrylic polymers and related compounds. The mat is then carried into a second bath containing zinc chloride or sodium chloride or another polyvalent cation which will coagulate the anionic resin droplets and deposit them on the fibers. The mat is then passed through a series of baths for removing the salt and the uncombined resins. From there the stock goes through a drying oven for the curing of the resin. The effluent from this process is the discharge from the wash bath after the coagulation and the discharge from the coagulating bath. The effluent will contain zinc chloride and a small quantity of the resin. Although the quantities of resin used are very high, and the final product may contain as much as 50 percent of the resin by weight, there is very little resin left in the wash water. This can be removed by centrifuging or filtration. The subject of the pollution load from the nonwoven industry is not dealt with in any of the usual texts or reports on the textile industry.

THE TREATMENT OF TEXTILE WASTES

The treatment of textile wastes is as varied as the wastes from the different textile plants. We have seen in the previous sections that the processing of cotton, wool and synthetics involve entirely different processes and as a result different types of pollution loads.

The wastes from cotton production include BOD, primarily from sizing and dissolved materials from the mercerization and cleaning processes. There are very little settleable solids and there is considerable material of a biologically refractive nature.

The main problem in the cotton effluent processing is the decrease in BOD and the eventual color removal. In wool effluent, the main causes of the problem is in the scouring of the wool in the production of wool tops. Dirt, grease and materials associated with the raw wool carry a tremendous pollution load, far greater than we find in any other phases of the textile industry.

The treatment of the pollution wastes from the wool plant, therefore, present entirely different problems than those observed in a textile mill concerned only with dyeing.

In the processing of synthetics, the pollution load is considerably lighter in that dye wastes are a prime consideration. Here there may be some specific toxic materials, but these will probably be eliminated or substituted for in the operation.

THE COTTON MILL WASTE TREATMENT

Treatment of cotton effluent would require all or some of the following processes:

Equilization - Equilization is necessary since the discharge from the kiering and desizing operations will yield intermittent slugs of highly caustic wastes. These materials should be added slowly. Such effects would be less objectionable whether the effluent is treated at the textile plant or the effluent becomes part of a municipal treatment plant.

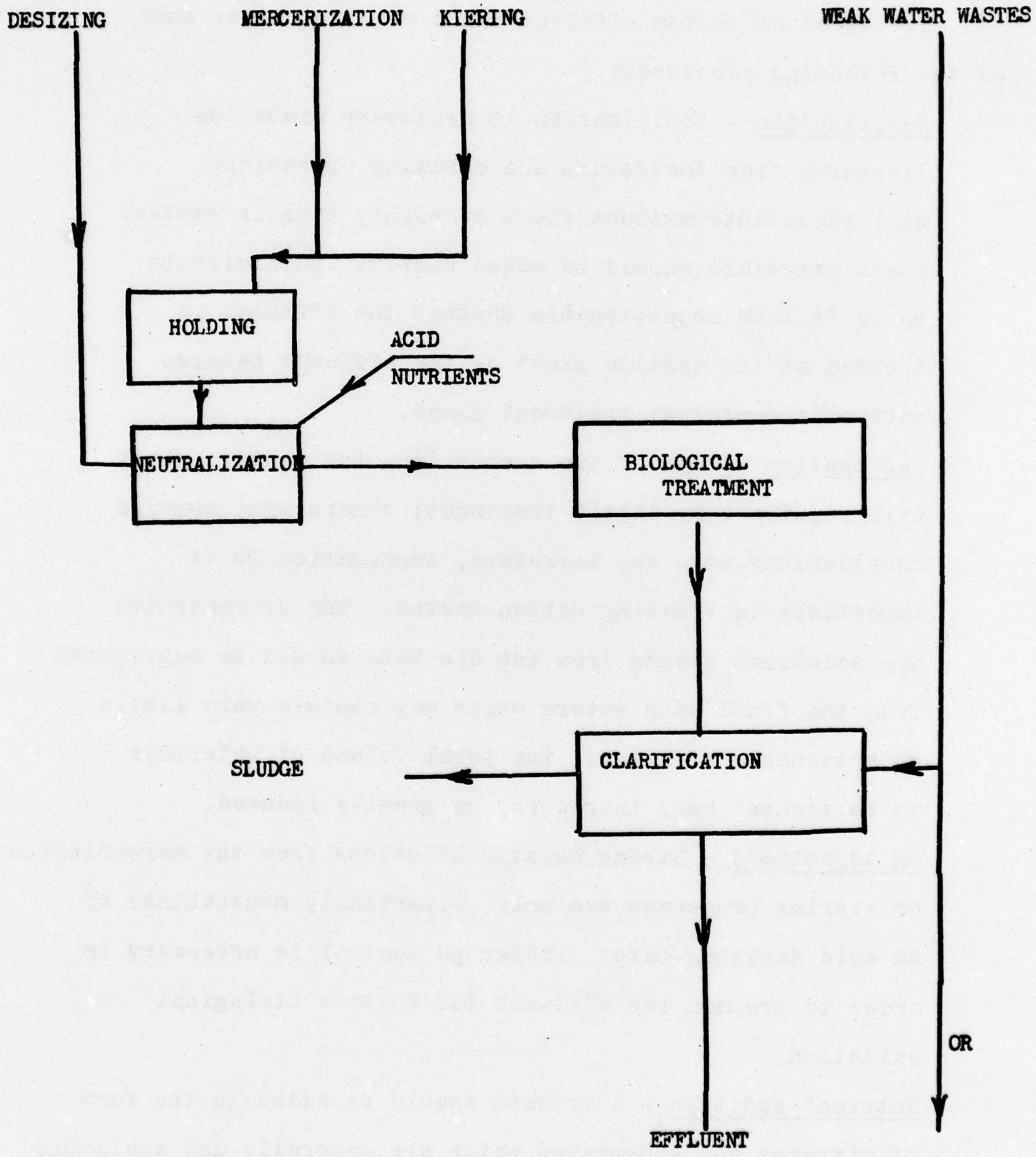
Segregation - Some of the wastes from the textile plant will require very little treatment; others will require considerably more so, therefore, segregation is of importance in treating cotton wastes. The concentrated dye solutions coming from the dye bath should be segregated from the final wash waters which may contain very little objectionable effluent. The total volume of materials to be treated can, therefore, be greatly reduced.

pH Adjustment - Strong caustic solutions from the mercerization or kiering processes can only be partially neutralized by an acid desizing bath. Proper pH control is necessary in order to prepare the effluent for further biological oxidation.

Nutrient Addition - Nutrients should be added in the form of nitrates and phosphates which are generally not available

COTTON EFFLUENT TREATMENT

STRONG WASTES



POLLUTANT REMOVAL IN COTTON AND SYNTHETIC TEXTILES *

REMOVAL METHOD	Removal Efficiencies, %		
	BOD	SS	TDS
SCREENING	0-5	5-20	0
PLAIN SEDIMENTATION	5-15	15-60	0
CHEMICAL PRECIPITATION	25-60	30-90	0-50
TRICKLING FILTER	40-85	80-90	0-30
ACTIVATED SLUDGE	70-85	85-95	0-40
LAGOON	30-80	30-80	0-40
AERATED LAGOON	50-95	50-95	0-40

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* From FWPCA, "The Cost of Clean Water", vol. III, Industrial Waste Profile No. 4, Textile Mill Products, September, 1967

in sufficient quantity to maintain proper biological oxidation. Proper balance need be maintained.

Biological Oxidation - Various biological oxidation treatments that can be used in textile wastes are similar to those in municipal sewage. These include trickling filter, activated sludge, lagooning or aerated lagoon. The choice of any one of these systems would depend upon the cost and the particular problems of the individual plant. Aerated lagoons appear to be the most popular for the industry today.

WOOL PROCESSING

In the processing of wool wastes, a most important factor is the removal of the grease and suspended solids prior to the biological treatment. Wool wastes would be combined as they came from the various washes and the grease recovery plant indicated on Page 15.

The first step is the additional grease recovery. This can be accomplished by the addition of acid which will neutralize the carbonate and soaps and cause the grease emulsion to break and grease to float to the top. Grease could also be recovered by a centrifuge. In either case the grease recovered at this point would be sent back to the purification plant for the recovery of the lanolin.

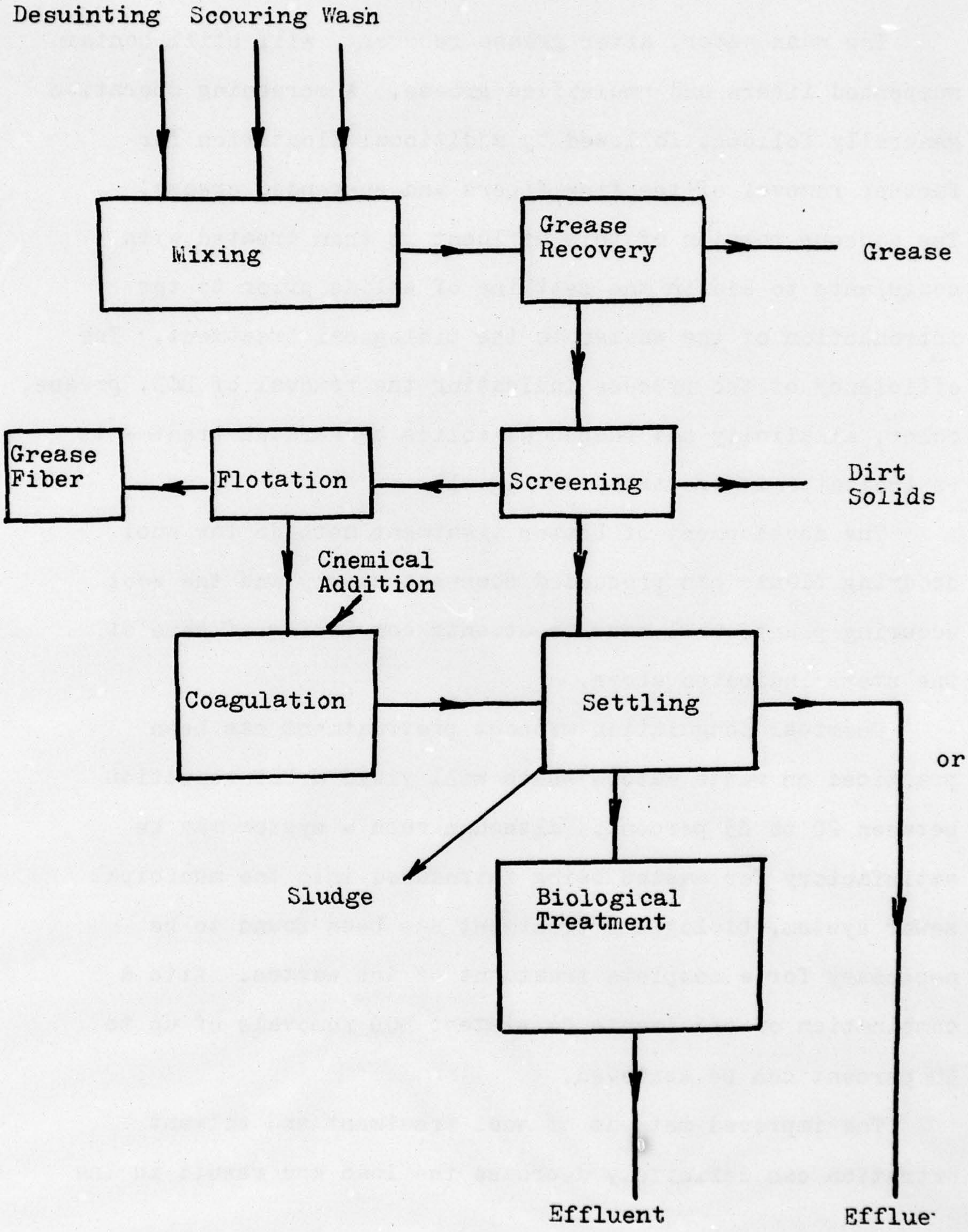
The wash water, after grease recovery, will still contain suspended fibers and emulsified grease. A screening operation generally follows, followed by additional floatation for further removal of the fine fibers and suspended grease. The aqueous portion of this effluent is then treated with coagulants to aid in the settling of solids prior to the introduction of the wastes to the biological treatment. The efficiency of the process indicating the removal of BOD, grease, color, alkalinity and suspended solids by various treatments is indicated in the table on Page 15.

The development of better treatment methods for wool scouring plants has proceeded somewhat slowly and the wool scouring plants will have treatments consisting of some of the steps indicated above.

Chemical coagulation without pretreatment has been practiced on waste waters which will yield a BOD reduction between 20 to 85 percent. Although such a system may be satisfactory for wastes being introduced into the municipal sewer system, biological treatment has been found to be necessary for a complete treatment of the wastes. With a combination of treatments consistent BOD removals of up to 90 percent can be achieved.

The improved methods of wool treatment and solvent extration can definitely decrease the load and result in the

WOOL TOP TREATMENT



POLLUTANT REMOVAL EFFICIENCIES IN WOOL TEXTILES *

Treatment Method	BOD	Grease	Color	Alkalinity	SS
	Normal reduction percent				
Grease Recovery					
Acid Cracking	20-30	40-50	0	0	0-50
Centrifuge	20-30	24-45	0	0	40-50
Evaporation	95	95	0	0	
Screening	0-10	0	0	0	20
Sedimentation	30-50	80-90	10-50	10-20	50-65
Flotation	30-50	95-98	10-20	10-20	50-65
Chem Coagulation					
$CaCl_2$	40-70				80-95
Activated Sludge	85-90	0-15	10-30	10-30	90-95
Trickling Filtration	80-85	0-10	10-30	10-30	90-95
Lagoons	0-85	0-10	10-30	10-20	30-70

* From FWPCA, "The Cost of Clean Water," vol III, Industrial Waste Profile No. 4, Textile Mill Products, September, 1967

recovery of solvent and a good quality lanolin. This can result in a possible recovery of the soap for reuse, and a definite decrease in the BOD load. The economics of this approach and the poor market for lanolin has been a drawback to this major development in improvement in wool processing.

The main hope for decreasing the pollution load in the cotton industry is in the reuse of process water. The reuse of caustic bearing rinse water from mercerizing is practical in some plants. Analysis and evaporation can concentrate the dilute caustic rinse water for subsequent reuse in mercerizing and kiering. It has been shown that after 85 to 90 percent of the BOD removal and activated sludge, the effluent water could be reused for rinsing, after bleaching.

Desizing by enzyme treatment results in some glucose with a possibility of recovering this glucose by multiple effect evaporation. This system, although technically feasible would probably not be economically feasible under present market conditions. There is a possibility of recovery of pectan waxes and other impurities from the cotton. These systems are under study and may prove to be technically and economically feasible.

TREATMENT OF DYE WASTES

The treatment of dye wastes, whether they come from cotton, wool or synthetics have the same general characteristics. The dye and finishing processes produce materials of intense color, fairly high BOD and practically no settable solids.

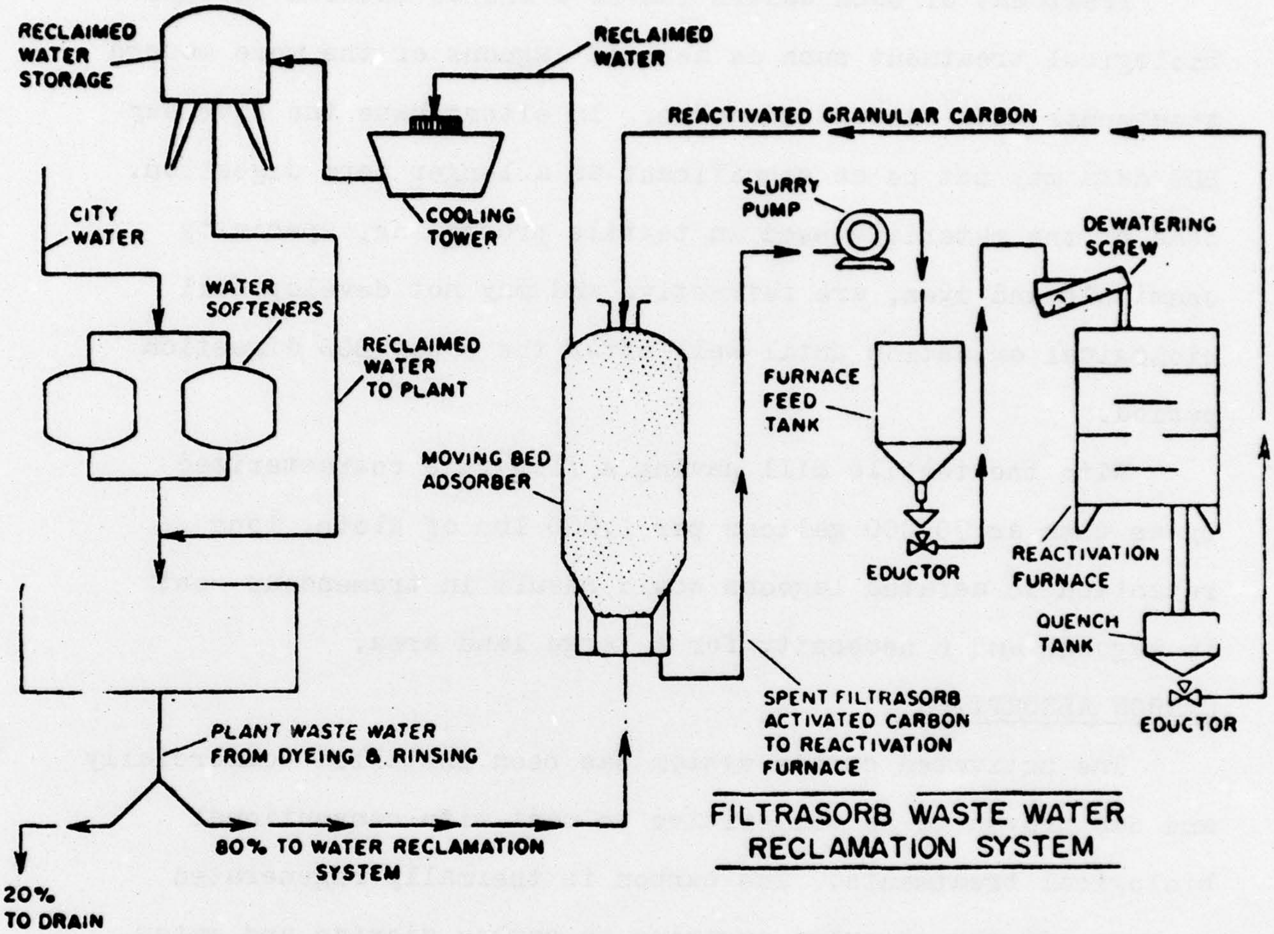
Treatment of such wastes leaves a choice between extensive biological treatment such as aerated lagoons or the more modern treatments with activated carbon. In either case the five day BOD data may not be as significant as a longer term digestion. Some of the materials used in textile processing, specialty chemicals and dyes, are refractive and may not develop full biological oxidation until well after the 5 day BOD digestion period.

With the textile mill having a flow rate characterized by as much as 70,000 gallons per 1,000 lbs of cloth, long retention in aerated lagoons would result in tremendous cost in lagoons and a necessity for a large land area.

CARBON ABSORPTION

The activated carbon system has been installed commercially and has proven to be competitive in cost with conventional biological treatments. The carbon is thermally regenerated to burn off the absorbed organics to carbon dioxide and water. There is no biological sludge formed in the process, so solids waste disposal is minimized and space is saved. A flow diagram of the activated charcoal system and the performance characteristics are given on the following page.

The system has the added advantage of producing no sludge. The initial cost of the system is very high but the lower operating costs and small land area needed make this an attractive system when relatively small volumes of effluent are to be processed.



FILTRASORB WASTE WATER RECLAMATION SYSTEM

ACTIVATED CARBON EFFLUENT TREATMENT PERFORMANCE *

	Dyehouse wastewater influent	Treatment Plant effluent	Reduction %
COD-mg/l			
at 8.5 gpm/ft^2	945	178	81.1
at 15.6 gpm/ft^2	550	280	49.0
TOC-mg/l			
at 8.5 gpm/ft^2	378	78	81.7
at 15.6gpm/ft^2	220	115	47.8
Color			
at 8.5gpm/ft^2	--	--	99.4
at 15.6gpm/ft^2	--	--	99.5

Courtesy Am. Dyestuff Reporter, June, 1971

COSTS

An accurate estimation of the treatment of textile wastes is not available since the most effective treatments are too new. As a rough estimate of costs of waste treatments, we are including two graphs from a recent book by Eckenfelder. The relative relationships between the capital costs and the extent of treatment are easily seen from these data.

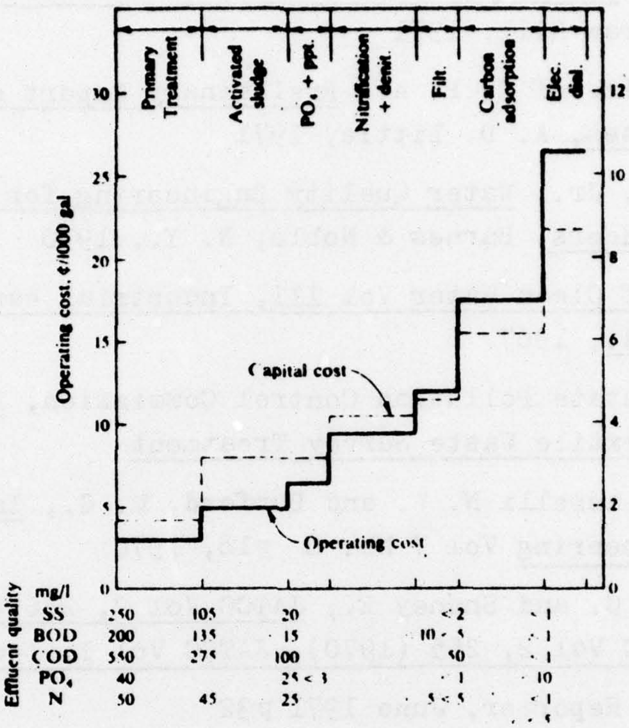


Figure 13.14 Relationship between effluent quality and capital and operating cost—muncipal sewage.

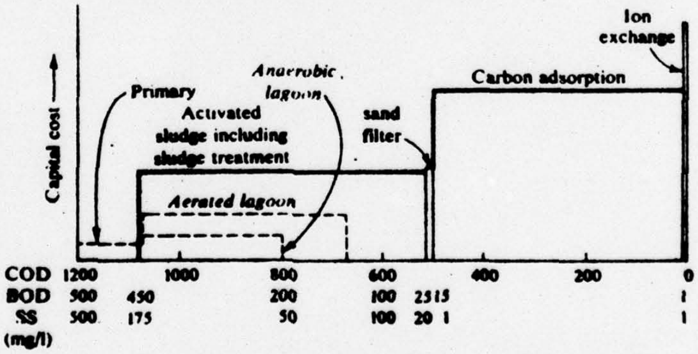


Figure 13.15 Capital cost of treatment plant vs. effluent quality vs. waste removal—chemical industrial waste.

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THE NATURE AND TREATMENT
of
TANNERY EFFLUENT

Prepared for

U. S. Army Corps of Engineers

by

THORSTENSEN LABORATORY

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NO. 21351

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SIDE UPPER LEATHER

The manufacture of side upper leather is the largest single segment of the leather industry in the United States. Of the 40 million cattlehides available a year, 15 to 18 million are made into shoe upper leather. An additional 2 to 3 million hides are made into sole leather and the remainder of the hides are exported onto the world market. The shoe and leather industry in the United States has been a bit depressed lately because of the import competition. The larger, more progressive companies with better capitalization are doing good business but marginal companies have a hard time of it.

In the Merrimack Valley there are several large side upper leather tanneries. Approximately 10% of the side upper leather industry is concentrated in this area. The production size of the tanneries involved is measured in the number of hides that are processed. A large tannery may produce as much as 2,000 hides a day and a small tannery would produce about 300 hides per day. A company will employ approximately 100 people for every 500 hides processed. The total quantity of water used is approximately 8 to 12 gallons per pound of hide. A general description of processing methods is given below which will be used in conjunction with a block disgram outline of the sources of waste in the tannery effluent of a tannery making side upper leather.

SOAKING

The hides received by the tannery are green salted cattlehides, usually from the Midwest. These hides will average about 60 pounds each and contain about 40% moisture and 15% salt. The hides are cured by salt at the packing company for preservation in shipping. Hides are soaked by tumbling in drums with flowing water to wash out the salt, manure, soluble proteins, blood, dirt and other materials. This one operation is one of the major causes of pollution from a tannery.

The soaked hides are then trimmed and fleshed. Fleshing is a mechanical scraping of the flesh side to remove excess flesh and unwanted adhering matter. The hides are then unhaired.

UNHAIRING

Unhairing is done by soaking the hides in a solution of lime containing strong reducing agents such as sodium sylfhydrate, dimethylaminesulfate and similar materials. The liming causes a loosening of the hair and, in the hair destruction system, it may break down the hair and break it into small particles. After liming, the hides are washed to remove the adhering chemicals and the protein degradation products.

The washing and liming effluent also contains lime, sulfides, protein degradation products, some fatty soaps from the saponification of the fats during the liming, hair particles, etc. This liming solution will have a pH of near 12.

After liming the hides may be fleshed again and then sent for the bate, pickle and tan process. There are, of course, variations in process from one company to another and modifications in formulations in which the hair is saved, and the amount of fleshing done.

Some tanners both lime flesh and soak flesh and others limit their fleshing to the lime flesh only. The flesh that is taken off amounts to about 15% of the weight of the hides. Some tanneries have found it profitable to render these fleshings to recover the grease. In these cases, the fleshings may be sent to the effluent stream as a partially digested protein. In other cases, fleshings are disposed of by hauling to a land fill disposal system. The disposal of fleshings is a major problem for tanneries.

BATE, PICKLE OPERATION

The limed hides are put into a drum for the bate and pickle operation. Bating is a treatment of the hide with deliming materials such as ammonium sulfate, some acids and enzymes. The purpose of the enzymes is to break down some unwanted proteins, clean up the surface of the skin, and help soften the leather. The bating process is usually carried on as a part of the pickling process. In pickling, hides are washed after bating and brine is added to maintain a salt concentration of approximately 5% NaCl on a solution basis. Sulfuric acid is added. The pH of the hides is brought to about 2 for chrome tanning. The effluent from the above process contains ammonium sulfate, some of the degradation products from the hide, fats and considerable quantities of salt. The pH is very low, probably between 2 and 3.

CHROME TANNING

This part of the production is usually combined with the bate, pickle and tan operation in many tanneries. We separate it, however, since there will be information on some tanners who buy hides in the pickled state.

The chromium salts, sodium chloride, perhaps some acid, and masking materials are added in this process and it is here that the hide becomes leather. Also, the protein materials become stabilized against bacterial attack. The degradation products coming from this procedure are sodium chloride and chromium salts. The final pH will be about 4.

Chrome tanned leather is sent through a belt knife for leveling the thickness and later sent through a shaving machine which mills the leather to an accurate thickness. Considerable quantities of shavings (about 2% of the hide weight) result from this operation. The shaved hides are then graded for different types of leather and sent for the retan, fatliquoring and coloring processes.

RETAN, COLORING AND FATLIQUORING

The retanning operation treats the hides with vegetable tanning materials (plant extracts). The color is brought about by acid type AZO dyes (primarily acid) and the fatliquoring or lubrication of the leather is done by treating the leather with oils in an emulsion. The oils are usually sulfated or sulfonated oils. The effluent from these processes varies a great deal depending on the type of leather being made, but it usually consists of spent dyes, spent tanning materials and a small quantity of oil. The leather is usually dried after this by paste drying.

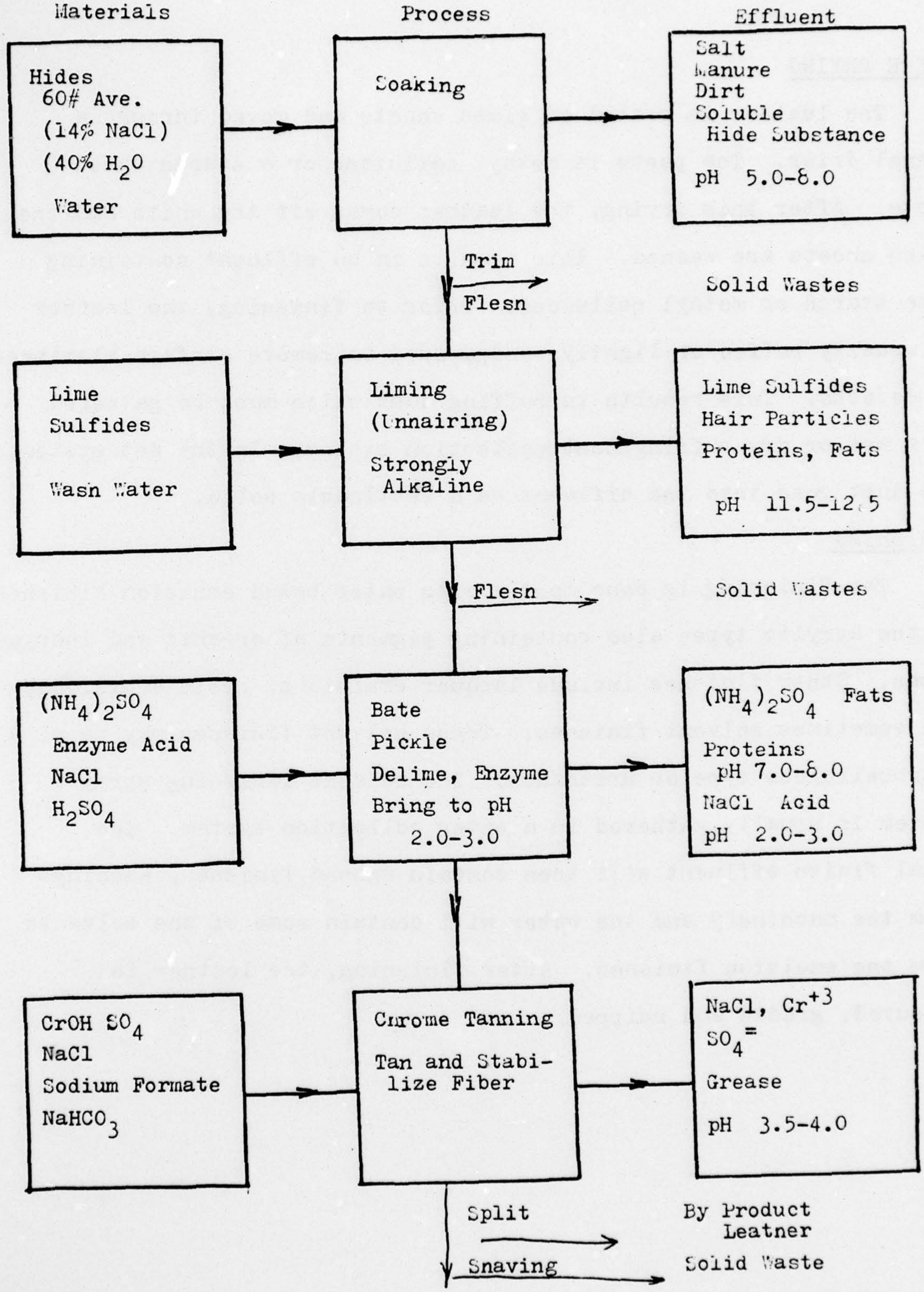
PASTE DRYING

The leather is pasted on glass sheets and moved through a tunnel drier. The paste is methyl cellulose or a starch based paste. After this drying, the leather comes off the units and the glass sheets are washed. This results in an effluent containing some starch or methyl cellulose. Prior to finishing, the leather is usually buffed or lightly sandpapered to remove surface blemishes or defects. This results in buffing dust which must be gathered by a wet or dry buffing dust collection system. In the wet system, the dust goes into the effluent as a settleable solid.

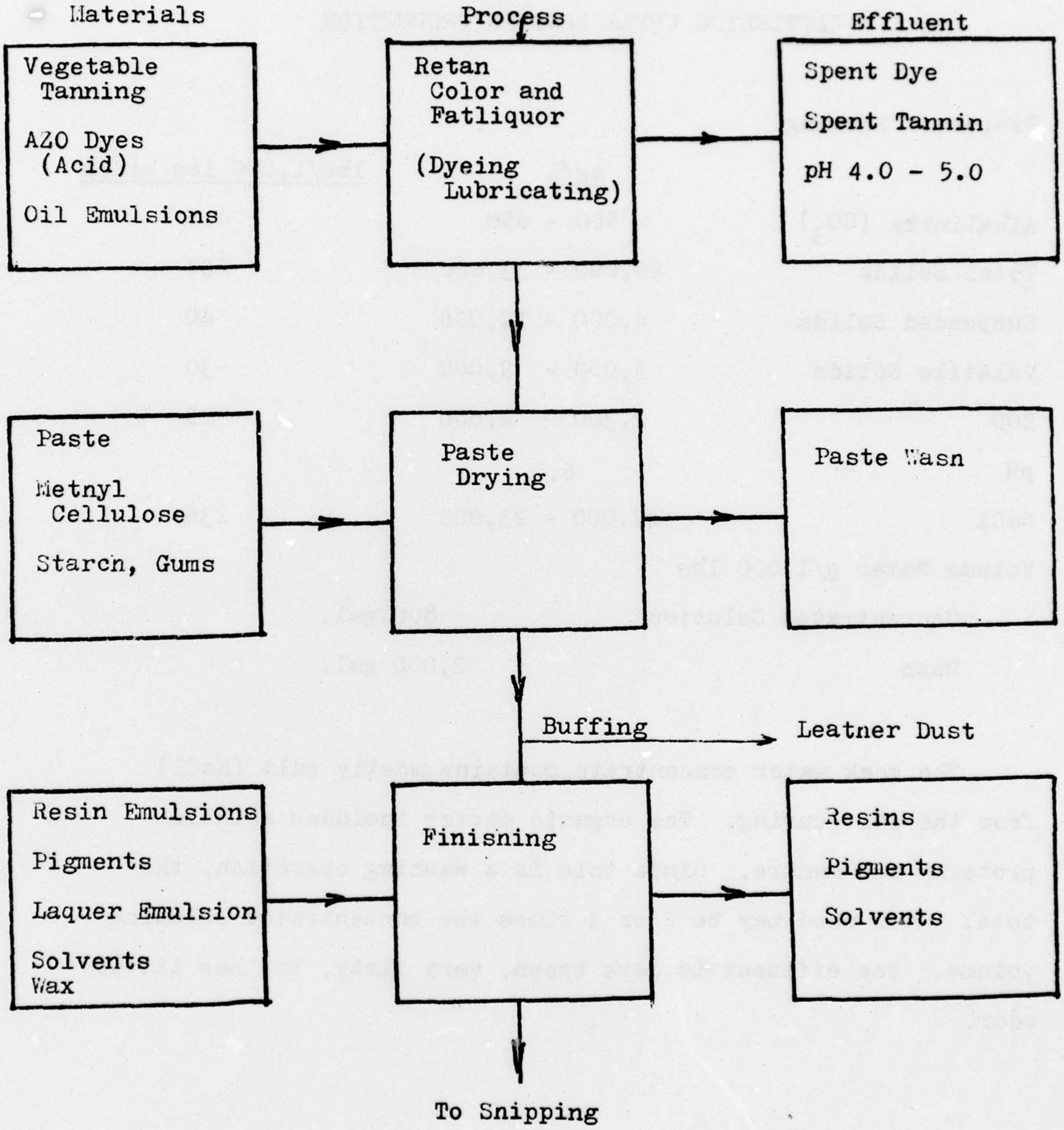
FINISHING

The finishing is done mostly with water based emulsion finishes of the acrylic types also containing pigments of organic and inorganic types. Other finishes include lacquer emulsions, resin emulsions, and sometimes solvent finishes. These solvent finishes may be of a nitrocellulose type or urethanes. The solvent finishing spray system is usually gathered in a water collection system. The final finish effluent will then contain unused finishes, washings from the machinery and the water will contain some of the solvents from the emulsion finishes. After finishing, the leather is measured, graded and shipped.

FLOW SHEET SIDE UPPER LEATHER



FLOW SHEET SIDE UPPER LEATHER



COMPOSITION OF CONCENTRATED SOLUTIONS

CATTLEHIDE UPPER LEATHER PRODUCTION

Process: Soaking

	mg/l	lbs/1,000 lbs hides
Alkalinity (CO_3)	500 - 650	4.5
Total Solids	25,000 - 33,000	204
Suspended Solids	4,000 - 10,000	40
Volatile Solids	3,000 - 9,000	30
BOD	2,300 - 2,600	15
pH	6.5	
NaCl	19,000 - 23,000	136

Volume Water g/1,000 lbs

Concentrated Solution	800 gal.
Wash	2,000 gal.

The soak water concentrate contains mostly salt (NaCl) from the salt curing. The organic matter includes soluble proteins and manure. Since this is a washing operation, the total water used may be 2 or 3 times the concentrated solution volume. The effluent is dark brown, very dirty, but has little odor.

Process: Unhairing

	mg/l	lbs/1,000 lbs hides
Alkalinity (CO_3)	13,000 - 26,000	54
Total Solids	70,000 - 85,000	210
Suspended Solids	13,000 - 18,000	40
Volatile Solids	12,000 - 25,000	48
BOD	10,000 - 20,000	40
pH	11.0 - 12.0	
NaCl	15,000 - 22,000	45
$S^=$	3,000 - 4,000	10
Volume Solution	Concentrated	300-400 g/1,000 lbs
	Wash	3,000 - 5,000 g/1,000 lbs

The concentrated unhairing wastes are the largest problem of the side leather tanning effluent. The BOD represents approximately 50% of the total BOD produced. The large volume of wash water used is to remove the sulfides and surface dirt. The sodium chloride is from the carry over from the soaking. The effluent is blue-white very dirty and has a bad odor.

Process: Bate and Pickle

Bate Liquors

	mg/1	lbs/1,000 lbs hide
Alkalinity (CO_3)	2,500 - 3,000	7
Total Solids	11,000 - 17,000	37
Suspended Solids	5,000 - 8,000	18
Volatile Solids	6,000 - 10,000	21
BOD	4,000 - 9,000	13
pH	7.5 - 9.0	
Ammonium Nitrogen	2,000 - 2,500	10

Volume Solution/1,000 lbs hides

Concentrate	300 - 400 g
Wash	500 - 600 g

Bate wastes are high in ammonium nitrogen due to the use of ammonium chloride in the process. The effluent is slightly milky, and may have an odor of ammonia or sulfide.

Process: Pickle Liquors

	mg/l	lbs/1,000 lbs hide
Acidity	2,000 - 3,000	3
Total Solids	65,000 - 80,000	70
Suspended Solids	5,000 - 8,000	7
Volatile Solids	6,000 - 8,500	7
BOD	2,500 - 3,000	3
pH	2.5 - 3.0	
NaCl	45,000 - 50,000	50

Volume 130 g/1,000 lbs

Wash 0

There is no wash from a pickle solution. The pickle may be one step in a bate - pickle and tan operation. Some tanneries start with pickled hides and skins. Others may dump part of the pickle solution to adjust liquid levels. The effluent may be slightly milky but clear in color. The odor is very mild.

Process: Chrome Tanning

	mg/l	lbs/1,000 lbs hide
Acidity	3,500 - 5,000	8
Total Solids	85,000 - 100,000	180
Suspended Solids	12,000 - 18,000	28
Volatile Solids	10,000 - 14,000	24
BOD	1,800 - 2,400	4
pH	3.5 - 4.0	
NaCl	30,000 - 40,000	70
Cr^{+3}	6,000 - 8,000	15

Volume
200-300 g/1000 lbs

The chromium salts used in the tanning may be fixed to the extent of 50 to 75%. In the latest equipment, more concentrated solutions are used and efficiencies of up to 90% fixation may be obtained.

The data on sheepskin tannage is essentially the same as this. The effluent is dark blue-green in color, contains suspended fats and has a distinctive odor.

Process: Spent Color and Fatliquor

	mg/l	lbs/1,000 lbs of hide
Alkalinity	0	0
Total Solids	9,450	150
Suspended Solids	745	12
Volatile Solids	5,500	90
BOD	500 - 1,000	12
pH	3.60	

Volume

Concentrate	2,000 gal/1,000 lbs
Wash	2,000 g/1000 lbs

Color and fatliquor formulae vary greatly from tannery to tannery. The above data is an estimated average from a variety of processes studied by this laboratory. The effluent is usually cloudy and colored. The odor is not offensive.

Process: Pasting

	mg/l	lbs/1,000 lbs hide
Alkalinity mg/l $CaCO_3$	41.8	
Total Solids mg/l	428	.5
Dissolved Solids	228	.2
Volatile Solids	390	.4
BOD	1,000	1
pH	8.8	

Volume 120 gal/1,000 lbs hides

The effluent from the pasting unit is very small relative to the rest of the tannery. The effluent is milky but odorless.

Process: Finishing Room

	mg/l	lbs/1,000 lbs hide
Alkalinity	49.2	
Total Solids	768	10
Suspended Solids	284	4
Volatile Solids	520	7
BOD	1,043	15
pH	6.8	
Grease	92.7	1.3

Volume Solution 1,700 g/1,000 lbs hides

The finishing room data given above is based on one tannery analyzed by this laboratory. There will probably be large variations from tannery to tannery depending upon the finishing processes used. In most tannery effluent studies, the finishing room effluent is ignored as being too small to consider. The effluent is highly colored, cloudy, but without objectionable odor.

Total Waste Products from a
Side Upper Leather Tannery
lbs per 1,000 lbs of hide

	DATA I *	DATA II **
Total Solids	840	862
Suspended Solids	214	257
Volatile Solids	272	228
BOD	93	103
Waste Water Volume	10,100 gal	8,000 to 12,000 gal

Volume of sludge:	161 gal
$S^{=}$	3.4
Cr	21

Volume of water used: 8,000 - 12,000 gal/1,000 lbs

* From Water Pollution Control Series ORD-5

** From New England Water Pollution Control Commission Data

SHEEPSKIN SUEDE LEATHERS

One of the major types of leathers produced in New England is sheepskin suede. It is produced from pickled sheepskin, either from domestic or New Zealand sources. In the production of sheepskin the skins are unhaired at the source so that the wool can be sold separately in a wool pulling operation. The skins are then delimed, bated and pickled as with cattlehides as previously reported. The pickled sheepskins are then in a condition so that they can be held for storage, due to the seasonal nature of the sheep kill. The skins contain a large amount of grease and, therefore, the first step in production is the degreasing process.

DEGREASING

The skins are placed in a drum to which is added a solvent (approximately 50 gal/1,000 lbs) some wetting agents, water and salt. The salt is necessary to prevent the swelling of the skins. The effluent from this step contains grease, salt and solvent. It is also quite acid. The grease phase, with the solvent, is separated in most plants, distilled and the grease and solvent recovered for recycling. The detergent will continue with the water phase and be expelled with the effluent.

Chrome tanning of pickled sheepskins is done similarly to the outline given above on side leather. Salt, sulfuric acid and chromium salts are added and the chrome tanning salts combined with the sheepskin to form the leather.

Effluent discharge will include some spent chrome tanning salts, sodium chloride and some fats not removed during degreasing. These fats are materials that have not been removed during the degreasing. The chrome tanned leather is then fleshed by drumming the leather with some pumice and then mechanically removing the flesh on a rough wheel. The fleshings and pieces of pumice will result in an effluent which is a solid waste. Some pumice will remain with the skins and will come off in subsequent operations

RETAN AND FATLIQUORING

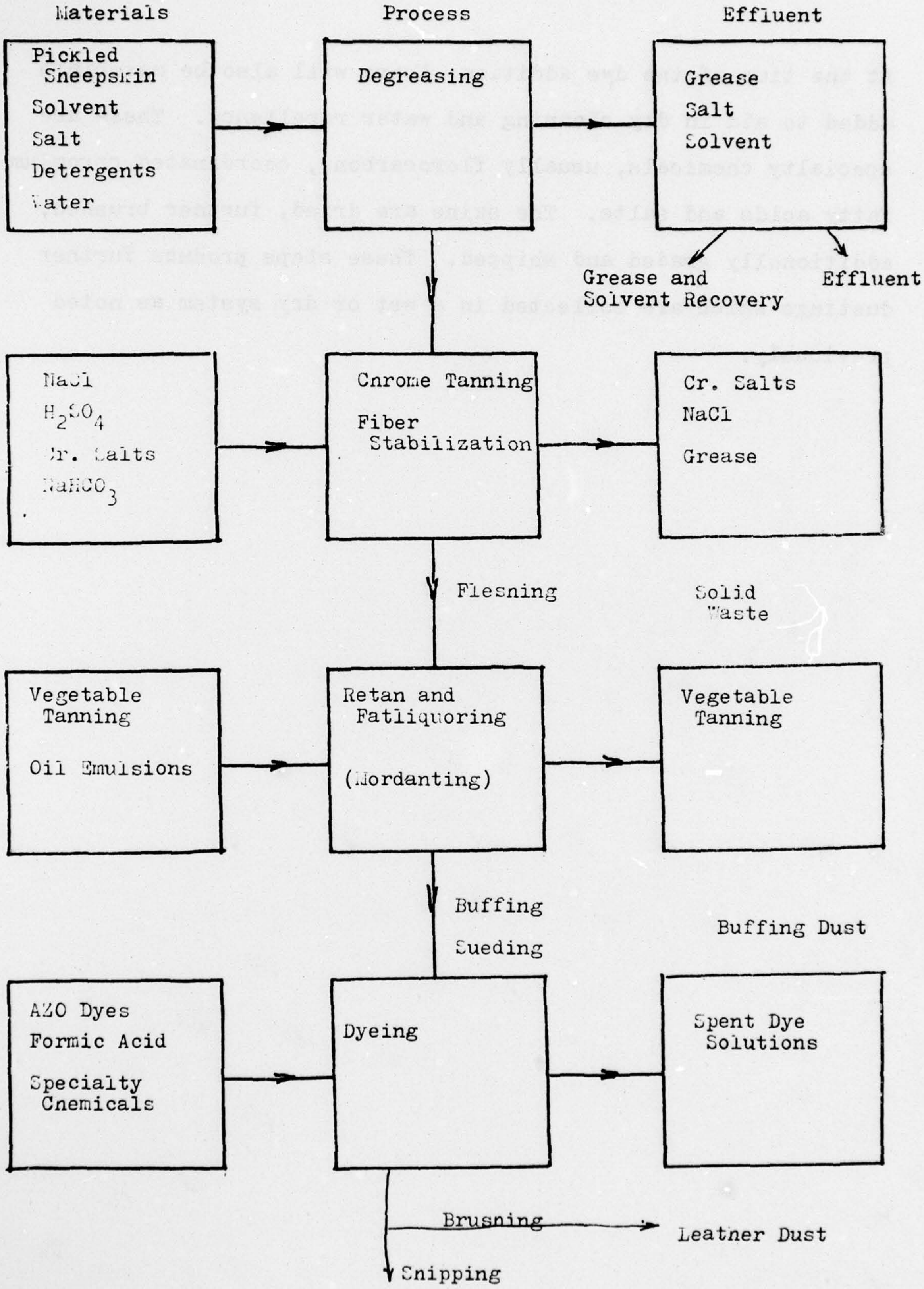
Retan and fatliquoring in the manufacture of garment suedes is used to make crust stock (similar to grey goods in textiles). Approximately 5% vegetable tanning materials and 10% fatliquor will be added to the skins. The fatliquor will be quantitatively removed from the skin. The retan operation will have a small amount of vegetable tan spent solution in it. The crusted skins are dried and buffed to develop the suede nap. The crusted skins are then dyed to the desired colors.

DYEING

The amount of dye needed will be between 1 and 15% (based on the weight of the crust leather), depending on the amount of color needed. The fixation of dye in chrome tanning will be less complete than in textiles since the temperatures involved cannot be as high. The spent dye solutions will retain some of the dye, usually about 5% of the original total and the solution will have a pH of about 4.

At the time of the dye addition, there will also be materials added to aid in dry cleaning and water repellency. These are specialty chemicals, usually florocarbons, coordinated chromium fatty acids and salts. The skins are dried, further brushed, additionally graded and shipped. These steps produce further dustings which are collected in a wet or dry system as noted previously.

FLOW SHEET SHEEPSKIN SUEDE LEATHER



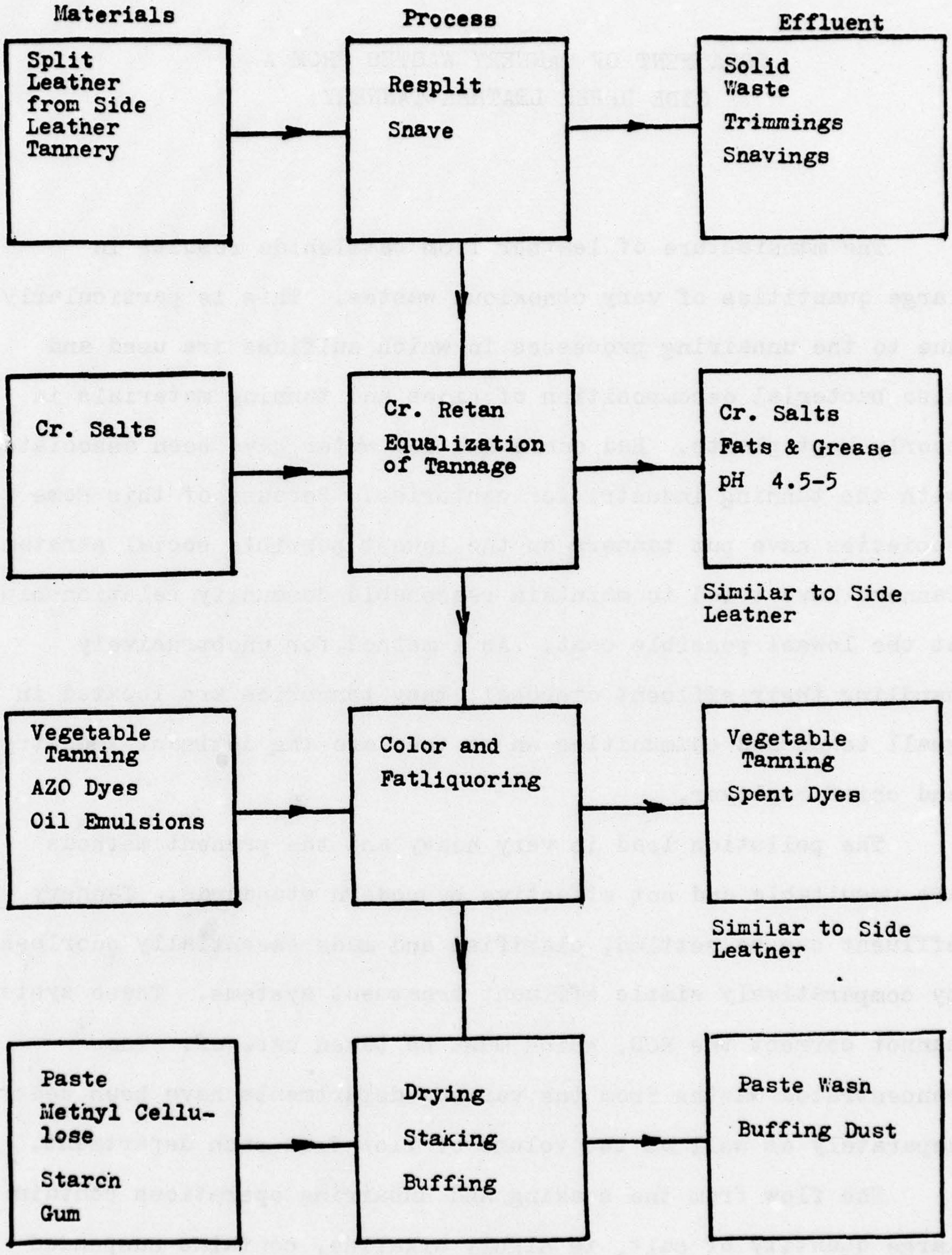
COMPOSITION OF EFFLUENT FROM A SHEEPSKIN TANNERY

	mg/l	lbs/100 doz skins
DEGREASING (AFTER RECOVERY)		
Salt	30,000	750
Fats & Solvent	2,000	50
pH	3.0 - 4.0	
BOD	2,000	50
Volume		3,000 gal
CHROME TANNING		
Salt	30,000	150
BOD	1,000	5
Cr	5,000	25
pH	3.5 - 4.5	
Fat	1,000	5
Volume		600 gal
RETAN AND FATLIQUORING		
BOD	2,000	20
pH	4.5 - 5.0	
Volume		1,200 gal
DYEING		
BOD	2,000	20
pH	4.0 - 4.5	
Volume		1,200 gal

SPLIT LEATHER

The splits removed from the side leather during the upper leather production are seldom completely finished by the side leather tannery. This is due to a difference in a marketing of the products. Split leather tanneries get the chrome tanned splits in a trimmed condition, from a side leather tannery. The splits may then be re-split or shaved to a uniform thickness and the edges trimmed. The shaved splits are then retanned, colored and fat-liquored similar to the side leather hides. The level of the dyes used in splits is considerably higher as a suede type leather is often made where a wide variety of bright colors is desirable. The spent solutions will contain chromium salts, vegetable tanning materials, dyes and some fats. Splits very often contain more fat than is desired and during tanning natural fats will come out and appear as scum. The splits are chrome retanned to bring them to a uniform chrome content. This results in some chromium salts being left in the effluent. Efficiency of take-up of the chrome tanning salts in a chrome retan operation is considerably less than the efficiency in a normal tanning operation. After dyeing and fatliquoring, the splits are dried and additional buffing is done, which results again in buffing dust. This will be collected in a dry or wet system. The skins are then ready for grading, measuring and shipping.

FLOW SHEET SPLIT LEATHER



TREATMENT OF TANNERY WASTES FROM A SIDE UPPER LEATHER TANNERY

The manufacture of leather from cattlehide results in large quantities of very obnoxioux wastes. This is particularly due to the unhairing processes in which sulfides are used and also bacterial decomposition of hides and tanning materials in poorly kept plants. Bad odors and bad water have been associated with the tanning industry for centuries. Because of this some societies have put tanners on the lowest possible social stratum. Tanners have tried to maintain reasonable community relationships at the lowest possible cost. As a method for unobtrusively handling their effluent disposal, many tanneries are located in small towns and communities where they are the dominant industry and chief employer.

The pollution load is very heavy and the present methods are unsuitable and not effective by modern standards. Tannery effluent can be settled, clarified and made essentially odorless by comparatively simple effluent treatment systems. These systems cannot correct the BOD, which must be taken care of. The concentrated wastes from the various departments have been described separately as well as the volume of flow from each department.

The flow from the soaking and unhairing operations contains a large quantity of salt, is highly alkaline, contains suspended particles of flesh, hair, dissolved proteins, dissolved fats and soaps.

These materials are usually sent through a screen to remove the gross particles,and all particles $\frac{1}{4}$" in diameter are removed by the screening system. For some tanneries this is the full extent of the effluent treatment.

The lime unhairing system creates sufficient alkalinity to dominate the entire tannery effluent, and if no further pH adjustment is made and complete equalization is obtained, the waste will usually maintain a pH above 10. One of the main concerns is that the pH will drop below 9½ or 10 and release hydrogen sulfide gas. On this basis, a number of tanneries have installed automatic pH control for the introduction of lime or sodium hydroxide into the effluent to maintain the pH.

The acid wastes from the bate, pickle and tan operations as well as those from the retan and dye operations can be mixed with the alkaline waste from the unhairing. This results in the clarification of the solutions by mutual precipitation. Spent chrome tanning liquors contain trivalent chromium sulfate and are acid. The spent retan and coloring solutions contain anionic vegetable tanning materials as well as acid dyes. These materials also will react with the basic solutions from the lime unhairing and through their neutralization, the proteins and other materials will approach their isoelectric point and aid in precipitation.

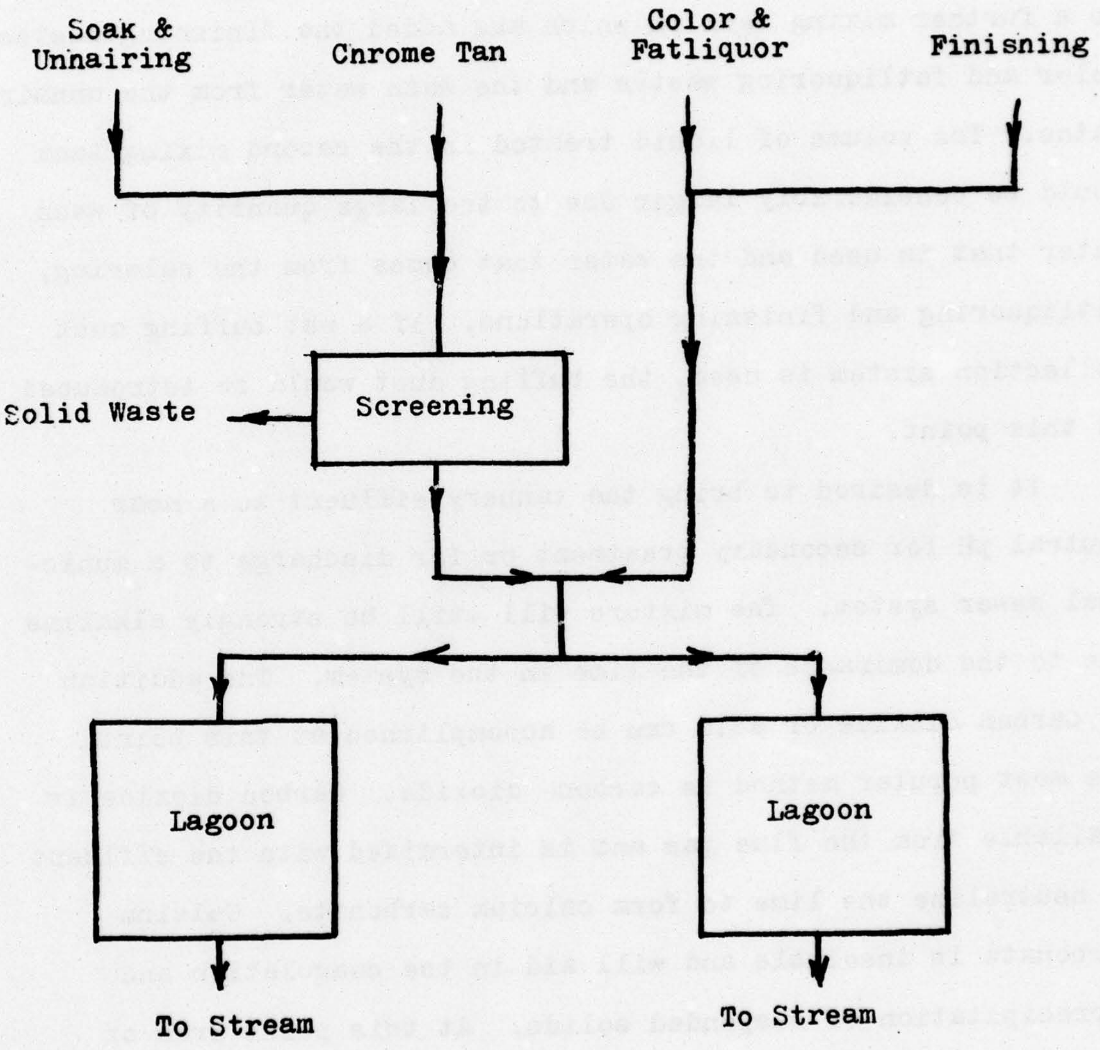
One of the standard practices in the industry could be to use two large lagoons and alternate their use and collect the bottom sludge. The sludge can be removed, after draining and drying, by physical means and carried off for land fill. This is the extent of the usual treatment of tannery wastes but does not represent the most modern systems or complete effluent systems. The effectiveness of this system can be seen at the end of the primary settling in the Table on Page 30.

TREATMENT OF TANNERY WASTES

From the data given we see that the tannery wastes are mostly due to the soaking and unhairing operations. In these processes with the degradation of hair and the release of large quantities of soluble protein material, a very heavy sludge results. Practically all effective treatment practices of working tannery wastes involve a combining of the soak and unhairing wastes through a preliminary screening. A preliminary screening will result in the elimination of solids such as large pieces of hair and small bits of flesh.

Concentrated wastes are highly alkaline and they are sent to an equalizing tank. The bate and pickle wastes are strongly acid and contain a considerable quantity of fat and suspended solids. Since the rate of discharge of the unhairing solutions and the bate and pickle solutions are not the same, the two should be balanced so as to avoid the lowering of the pH to the point where hydrogen sulfide gas is released. The bate, pickle and tan wastes, therefore, can go into a holding tank and then be added to the concentrated soak and unhairing wastes for equalization. Equalization of the two wastes brings about a very good coagulation of

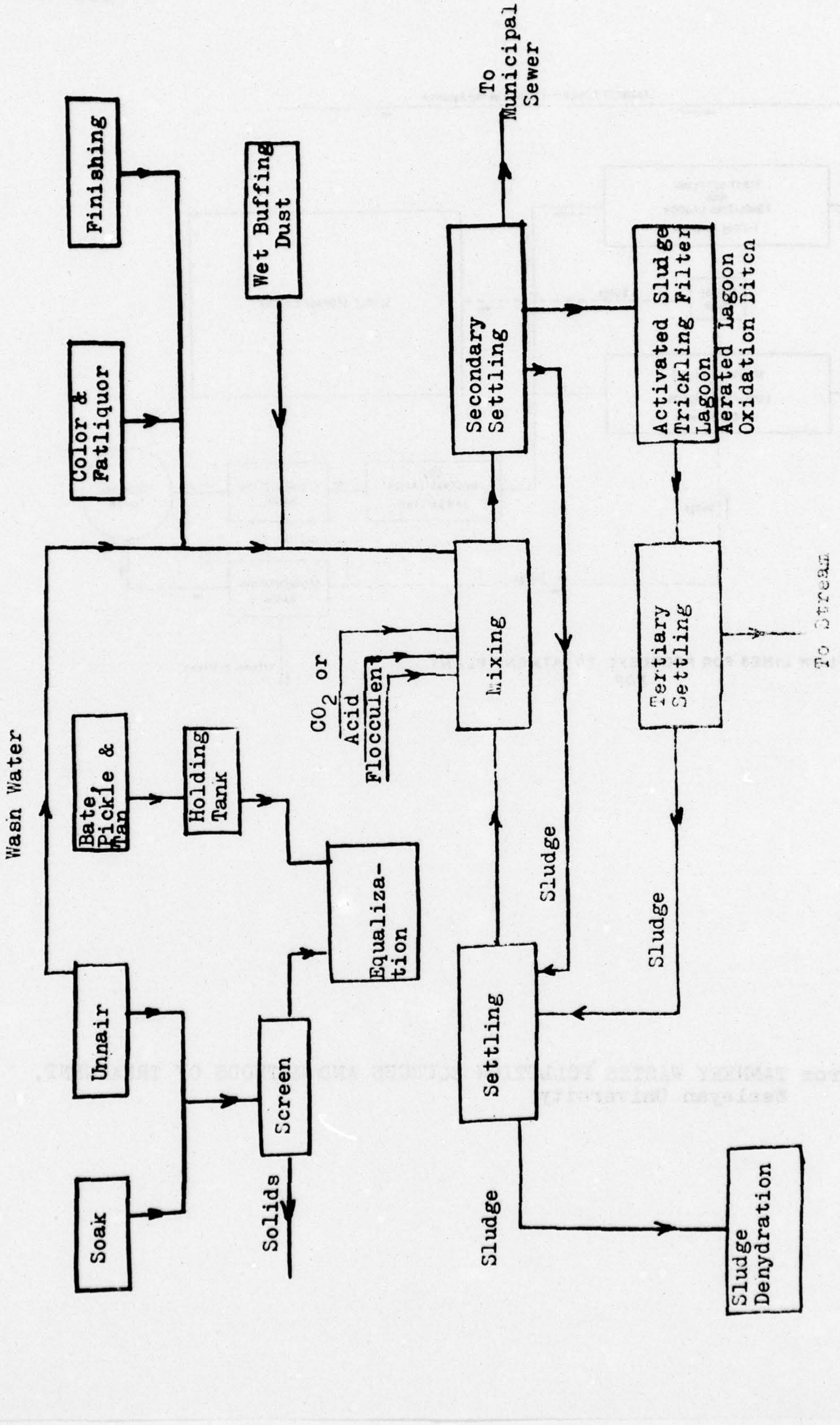
MINIMUM TREATMENT OF TANNERY WASTES

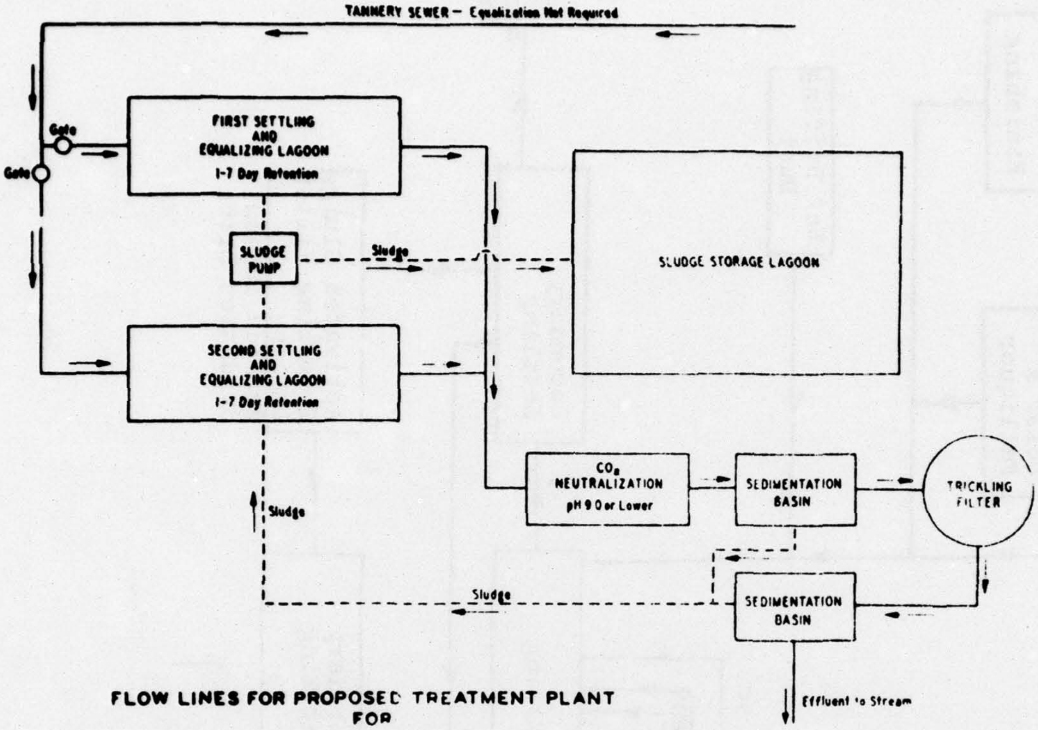


some of the suspended materials and will aid considerably in the settling of the sludge.

This preliminary settling will remove a large quantity of the suspended solids. The settled effluent can then be sent on to a further mixing tank in which are added the finishing wastes, color and fatliquoring wastes and the wash water from the unhairing baths. The volume of liquid treated in the second mixing tank would be considerably larger due to the large quantity of wash water that is used and the water that comes from the coloring, fatliquoring and finishing operations. If a wet buffing dust collection system is used, the buffing dust would be introduced at this point.

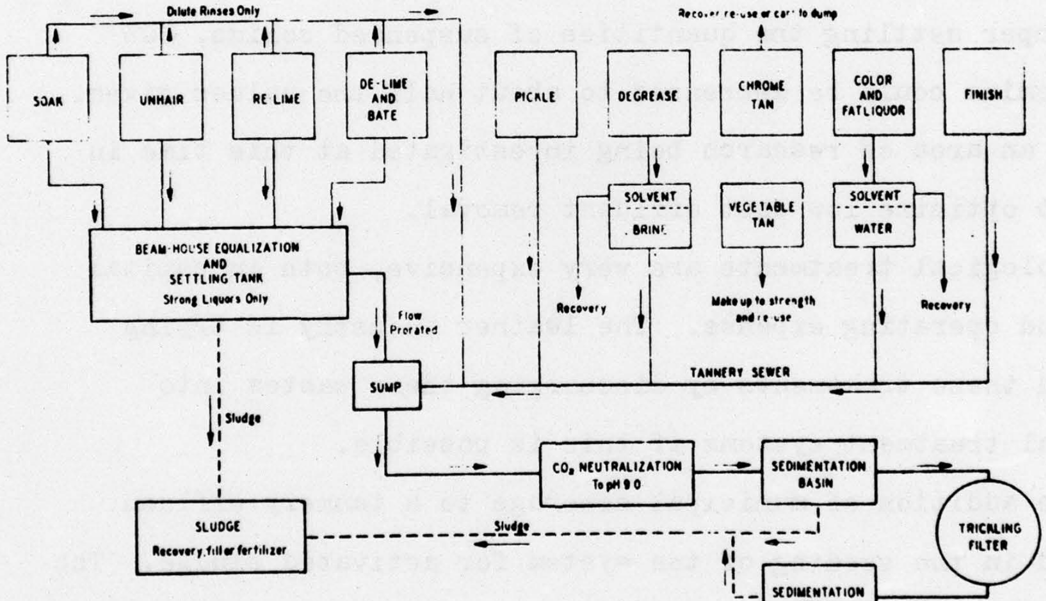
It is desired to bring the tannery effluent to a near neutral pH for secondary treatment or for discharge to a municipal sewer system. The mixture will still be strongly alkaline due to the dominance of the lime in the system. The addition of carbon dioxide or acid can be accomplished at this point. The most popular method is carbon dioxide. Carbon dioxide is available from the flue gas and is intermixed with the effluent to neutralize the lime to form calcium carbonate. Calcium carbonate is insoluble and will aid in the coagulation and coprecipitation of suspended solids. At this point iron or aluminum salts can be added to aid precipitation. Secondary settling can take place after this mixing for very effective removal of solids. The sludge from the secondary settling can be cycled back to the primary settling tank. This treatment


Soak
Unhair
Screen
Solids
Wash Water
Bate, Pickle & Tan
Holding Tank
Equaliza-tion
Color & Fatliquor
Finishing
Wet Buffing Dust
CO_2 or
Acid
Flocculent
Mixing
Settling
Sludge
Sludge
Secondary Settling
To Municipal Sewer
Activated Sludge
Trickling Filter
Lagoon
Aerated Lagoon
Oxidation Ditch
Tertiary Settling
To Stream
Sludge
Sludge Dehydration



FLOW LINES FOR PROPOSED TREATMENT PLANT
FOR

From TANNERY WASTES POLLUTION SOURCES AND METHODS OF TREATMENT,
Wesleyan University



FLOW LINES FOR PROPOSED TREATMENT PLANT
FOR
TANNERY WITH MINIMUM LAND AREA

FIGURE III

31

**From TANNERY WASTES POLLUTION SOURCES AND METHODS OF TREATMENT,
Wesleyan University**

up to this point would be the limit of the treatment if the effluent were going to a municipal sewer system. Solids would be rather effectively removed, but the solution would still contain almost half of the initial BOD. The biological treatment is much more expensive than the combining and settling systems of primary treatment, therefore, the biological treatment is avoided if at all possible.

The effluent at this point would be similar in composition to that shown after the carbonation treatment in the Table on Page 30. With proper settling the quantities of suspended solids, BOD and chromium could be decreased to about half the values given. This is an area of research being investigated at this time in order to optimize low cost effluent removal.

Biological treatments are very expensive, both in capital costs and operating expense. The leather industry is trying to avoid these treatments by discharging their wastes into municipal treatment systems if this is possible.

The addition of municipal sewerage to a tannery effluent will aid in the seeding of the system for activated sludge. The popularity of the various systems will depend upon the effectiveness that is needed and the cost. The simplest and cheapest is a lagoon system in which long retention times can be used. Retention times of up to 2 or 3 days are most common although the activated sludge system or trickling filter are much more effective.

DATA TAKEN FROM WPCR-ORD-5

	Plant Influent	Primary Settling Effluent	Carbonation	Activated * Sludge & Sec. Settling
pH Alkalinity	11.8	11.8	8.7	
Total Solids	5066	5100	5713	4230
Suspended Solids	872.8	540	436	372
Volatile Solids	990	1020	479	170
BOD	1531	800	630	49
$S^{=}$	93	83	64	1.5
Cr^{-3}	70	35	4.7	4.0
Settleable solids mg/l	10.8	2.14	.66	Trace

* Sanitary Wastes Added. Dilution to 150% by Sanitary.

Approximately half of the total solids that are found in tannery effluent is attributed to sodium chloride. Sodium chloride is not removed in any of the systems given and thus far the sodium chloride is gone through as a soluble solid completely through to the effluent stream. The concentration of sodium chloride in the effluent stream either with or without treatment will be approximately 5,000 mg per liter. The possibility of removing the sodium chloride from the effluent stream has not been considered in tannery waste studies to date. Sodium chloride could be removed from the final treated waste by ion exchange. The cost of such purification is very high, although data is not available at this time on tannery waste treatment.

Two materials that are found in the tannery effluent which are considered objectionable are sulfide and the chromium. Sulfide will gradually oxidize to sulfates and they will be effectively removed in the activated sludge system or any biological treatment. The most important consideration is that the pH of the tannery effluent containing the sulfides remain high enough to prevent the loss of hydrogen sulfide during the flow of the concentrated waste. It must be pointed out that the chromium used is trivalent chromium rather than hexavalent chromium. Hexavalent chromium is highly toxic. The toxicity of trivalent chromium is quite low. The spent chrome materials when mixed with the alkaline unhairing solutions precipitate as chromium hydroxide. This will act as a coagulant in the settling of solubilized proteins.

With an effective secondary settling system, the quantity of chromium in the solution can be dropped to less than 1 part per million. It is interesting to note that in Milwaukee, Wisconsin the sludge from the municipal sewage plant is processed into fertilizer. Milwaukee has several large tanning operations and we have found that the analysis of the fertilizer sold from the Milwaukee sewage treatment plant contains .25% chromium. This would indicate that there is no objectionable toxicity from trivalent chromium for irrigation purposes.

RENDERING OF FLESHINGS

Some tanners render the fleshings to recover the grease. The rendered fleshings is a profitable venture and an easy means of disposal of the fleshings. The common practice where this is being done is to run the rendered flesh water into the concentrated effluent stream and discharge it directly into the river. In the scheme outlined, the rendered fleshings would be removed partly by the screening and partly by the initial settling with sludge.

Rendering of fleshings contribute very highly to the BOD and the total suspended solids. In a complete waste treatment system, rendering of the fleshings would probably be kept completely separate from the liquid effluent disposal.

REMOVAL OF SLUDGE

The removal and concentration of sludge and tannery wastes has been a major problem. The sludge as settled contains about 7% solids and from a large tannery as much as 10,000 gallons a day could be obtained. Sludge can be concentrated by a vacuum filtration or by pressure filtration.

In either filtration system, the addition of the buffing dust from the dust collection system will act as a filter aid and allow much better concentration of the wastes. A sludge of as high as 40% solids can be obtained on a pressure filtration system. This solid sludge could be used for land fill or could be possibly used for a base material for fertilizer. Several fertilizer systems have been developed that are based on the use of tannery effluent.

SUBSTITUTION OF PROCESSED MATERIALS

The largest single contaminate in the tannery is the hide itself. Since most of the effluent in the tannery is due to the soaking, unhairing operations, it would be most desirable if these operations could be eliminated from the tannery. Hides that have been unhaired and have been treated through the pickle are in a stable condition of preservation being held at low pH and relatively high salt concentration. Pickled hides can stay in storage for as long as a year or more without bacterial degradation. This has been the accepted commercial practice in the sheepskin industry for many years.

Since pickled hides weigh less than green salted hides, the freight costs of shipping the hides in the pickle is considerably less and there are further advantages in that surface defects in pickled hides can be seen since the hair is removed.

The economic advantage of buying hides pickled results from the elimination of the salt curing step at the picking plant. There are several commercial pickling operations now working in the United States and it is expected that pickling will become a more acceptable commercial process in the future.

The technology of the unhairing and pickling operations is more complicated than the curing operations and its commercial acceptance has come slower than expected. For the tanner faced with an effluent problem, the purchase of pickled hides would be a solution to most of his problems, however, this shifts the effluent problem of the unhairing operation to the packing plant.

The relative impact of this effluent problem in an area where a large number of cattle are being slaughtered would be less than it would be in the usual New England communities with a tannery. Processing can be carried a bit further in that the hides can be not only pickled but also chrome tanned. In the chrome tanned state, many of the same advantages are obtained than we have from the pickle and one more step is eliminated from the tanner's operation, with a resulting labor saving and a decrease in the effluent problem.

Several commercial operations based on the manufacture of chrome tanned leather or "blue side leather" are now becoming commercial.

DETERGENTS

There has been a substitution in the wetting agents in detergents used in the leather industry toward the biodegradable materials. Phosphate based detergents have been all but eliminated and the wetting agents used in the tanning industry are limited almost entirely to the nonionic biodegradable type.

DISINFECTANTS

The disinfectants used are generally mixed chlorophenols as priority products. The tanning industry will probably continue to use these materials until such time as they are shown to be toxic and regulations would call for their elimination.

There is little hope of change of the process materials for low polluting process materials in the coloring, fatliquoring and finishing areas since these are minor pollutants in the consideration of tannery wastes.

REUSE AND RECYCLING

Possibilities for reuse and recycling of solutions in the tannery are quite good. In the manufacture of leather in the earlier processes years ago, the unhairing was conduced in vats and the solutions were reused and the amount of material dumped was considerably less.

In modern technology, to save labor, more concentrated solutions are used and it is necessary to wash rather thoroughly. The reuse of the lime unhairing system solutions is not being considered as a means of effluent removal in the modern leather industry due to high labor costs.

The wash water from the lime unhairing, however, could be used as a water supply for the soaking and unhairing operations, thus decreasing the total volume. The chrome tanning solutions could be collected separately, analyzed and recirculated. Systems of this type were developed during World War II for the saving of the valuable chromium salts at that time. In modern technology more concentrated solutions are used and these would adapt themselves better to the recycling processes. More effective *systems could be devised for the recovery of grease from the* spent solutions. Waste tannery grease has value for the manufacture of soaps and tanners' fatliquoring oils.
There is little possibility for recovery of spent materials and recycling in the coloring, fatliquoring and finishing operations.

COST OF TANNERY EFFLUENT TREATMENT

Cost of tannery effluent treatment has been estimated in the industrial waste profile for the Department of the Interior and the figures given in the tabulation on Page 39, indicate the cost of tannery effluent treatment by this study. An additional study of the activated sludge treatment as given by the water pollution control research series gives additional data on the cost of tannery effluent treatment. It is anticipated that complete treatment of tannery effluent would be between ½¢ a foot up to 1½¢ per sq foot of leather sold. The side upper leather sells for between 60¢ and 85¢ per sq foot on todays market. The cost of effluent treatment including the capital investment has proven to be too high for some tanners to accept and the effluent problem has resulted in the closing of some marginal tanneries in New England.

EFFLUENT TREATMENT FOR SHEEPSKIN LEATHER TANNERY

The sheepskin leather tannery has much less of a problem in effluent than a side leather tannery. Sheepskin leather tanneries are generally smaller than side leather tanneries, but they do not have the unhairing and soaking problems. The degreasing operations and the chrome tanning operations are possible causes of pollutants. The degreasing, if effectively run, will not result in a discharge of grease or solvents into the sewer. The solvent emulsion containing the grease can be broken effectively and distillation of the solvent for the recovery of the solvent and grease is essential for a profitable operation.

The waste discharges from a suede tannery will include the buffing dust and a relatively large amount of dye. For effective treatment of the effluent from this tannery, neutralization of the acid wastes should be accomplished and followed by a lagooning for the settling of the solids. The color, under these circumstances, will be eliminated and upon long standing the BOD will be greatly decreased.

SPLIT LEATHER TANNERY

The split leather tannery wastes are easier to handle than those from a sheepskin tannery. There is no degreasing operation or if a degreasing operation is used, then the quantity of degreasing material is less than in a sheepskin tannery. The effluent will be acid, will contain considerable quantities of dye, vegetable tanning materials and some chrome tanning salts. Effective neutralization of the wastes and settling should make this waste acceptable for a municipal treatment plant. The volume of effluent from a split leather tannery would probably be too small to warrant the introduction of the biochemical treatment process.

SOLE LEATHER

In the manufacture of sole leather severe pollution results. For the quantity of hides processed the pollution load is much greater than that found in a side upper leather tannery. Sole leather is made by the vegetable tanning process which results in a large discharge of spent vegetable tanning materials of high BOD.

There are no sole leather tanneries in the Merrimack basin so a discussion of sole leather tannery effluent would not be pertinent to the problems of this area. For this reason sole leather tanning was not included in this report.

COST OF TANNERY EFFLUENT TREATMENT

FROM FWPCA VOL III NO. 7

in $1000's

	Small 300 hides/day		Medium 300 hides/day		Large 300 hides/day	
	Capital Costs	Operating Year	Capital Costs	Operating Year	Capital Costs	Operating Year
Screening	2-13	.1-1.5	4-25	.3-3	10-60	1-9
Sedimentation	10-20	.45-1.5	20-40	1-3	45-100	2-6
Chemical Precipitation	10-80	1.5-7	20-160	3-15	45-100	9-45
Trickling Filter	27-80	1.5-4.5	50-150	3-10	100-300	7-25
Activated Sludge	34-100	1.5-8.0	75-250	3-16	150-500	7-40
Lagooning	2-5	.1-.6	5-10	.2-1.3	13-30	.5-3
Oxidation Point	3-7	.6-2	7-15	3-5	16-40	6-30
Sludge Disposal	----	1.5-7	----	3-15	-----	8-40

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THE NATURE AND TREATMENT
OF
PAPER EFFLUENT

Prepared for
U. S. Army Corps of Engineers

by
THORSTENSEN LABORATORY
Dr. Thomas C. Thorstensen

July 26, 1971

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TABLE OF CONTENTS

INTRODUCTION

The pulp and paper industry in the United States is the fifth largest industry in the value of assets and is tenth in the largest in value of shipments of manufactured goods. The quantity of paper produced is continually growing, but at the same time, the amount of waste produced per ton of paper is decreasing.

With expansion in the industry, the total amount of waste produced remains high with a total output of 3 billion pounds of suspended solids, 3 billion pounds of BOD carried in 960 billion gallons of water. Projected figures, taking into consideration that there have been changes in technology, indicate a growth rate of about 2% per year in all categories of waste loads and waste water quantities.

One of the major factors in pollution in the paper industry are the old mills. Paper mills were ideally located in forest mills to make use of the available pulp logs. The industry also requires tremendous quantities of water (up to as high as 50 thousand gallons per ton of fiber produced). When these mills were built, consideration was not given to the effect of the paper mill on the streams. Now these old plants with their heavy pollution loads are a serious problem. These mills are usually located in rural communities and small areas where they are the major employers.

Paper making may be divided into 2 major steps:

1. The preparation of the fiber, or purification of the fiber.
2. The assembly of the fiber into a useable form or final product.

The preparation of the fiber from the raw wood is called pulp making and the preparation of the fiber into the final product is called paper making.

PULP MAKING

Wood, as it is received, at the paper mill contains bark, surface dirt and heart wood. The surface dirt of the logs is removed by washing with water. The waste water from this washing is reused, if possible, as the grit and the bark are removed.

DEBARKING AND CHIPPING

The bark can be removed either by mechanical, hydraulic or chemical means. Debarking mechanically, means efficiency is low and the power consumption is high. By hydraulic means the log is debarked by the use of high pressure water jets. This uses considerable quantities of water, although most of this is recycled. Chemical debarking is a process, that is at present, in the experimental stage and has not been completely developed.

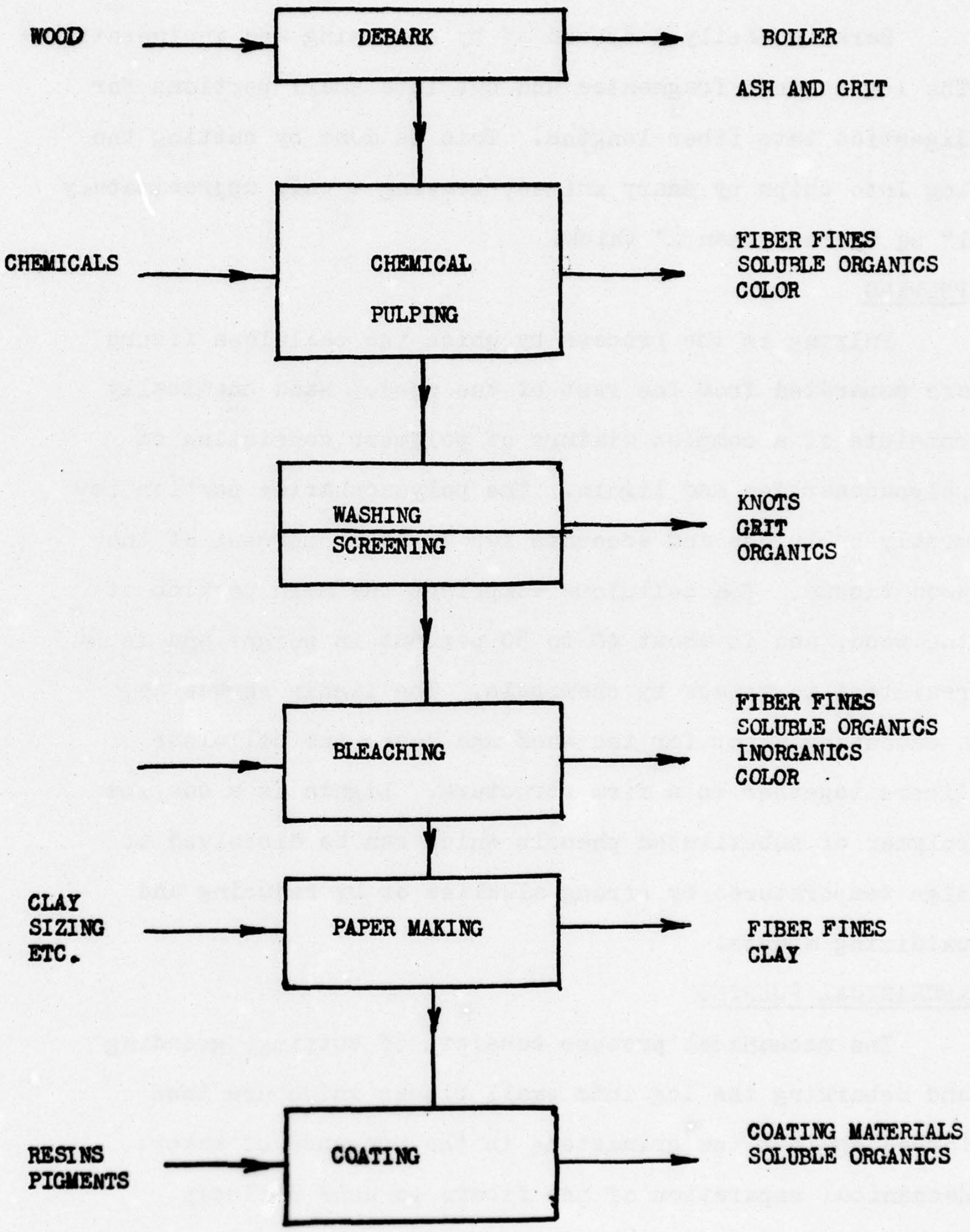
Bark is easily disposed of by screening and incineration. The log is then fragmented and cut into small portions for digestion into fiber lengths. This is done by cutting the log into chips by sharp knives, leaving a chip approximately 1" sq by less than ½" thick.

PULPING

Pulping is the process by which the cellulose fibers are separated from the rest of the wood. Wood chemically consists of a complex mixture of polymers consisting of polysaccharides and lignin. The polysaccharide portion is mostly cellulose and accounts for 70 to 80 percent of the wood tissue. The cellulose comprises the main portion of the wood, and is about 40 to 50 percent in weight and is resistant to attack by chemicals. The lignin serves as a cementing agent for the wood and keeps the cellulose fibers together in a firm structure. Lignin is a complex polymer of substituted phenols which can be dissolved at high temperatures by strong alkalies or by reducing and oxidizing agents.

MECHANICAL PULPING

The mechanical process consists of cutting, grinding and debarking the log into small blocks which are then forced against the grindstone in the presence of water. Mechanical separation of the fibers is done strictly


WOOD
DEBARK
BOILER
ASH AND GRIT
CHEMICALS
CHEMICAL PULPING
FIBER FINES
SOLUBLE ORGANICS
COLOR
WASHING
SCREENING
KNOTS
GRIT
ORGANICS
BLEACHING
FIBER FINES
SOLUBLE ORGANICS
INORGANICS
COLOR
CLAY
SIZING
ETC.
PAPER MAKING
FIBER FINES
CLAY
RESINS
PIGMENTS
COATING
COATING MATERIALS
SOLUBLE ORGANICS

mechanically and only the poor grade quality papers can result from this system.

CHEMICAL PULPING

The principle chemical processes in paper making are the sulfite, sulfate (kraft) and soda process. The systems are based on dissolving the lignin sufficiently so that the fibers can be separated. All use heat, pressure and highly concentrated solutions.

SULFITE PROCESS

The sulfite process consists of digestion of the wood chips in a solution containing bisulfite and an excess of sulfur dioxide. The reaction of the sulfite with the lignin aids in the solubilization of the lignin and splits the lignin cellulose complex. This process yields pulp which is good for bleaching, which gives a high degree of brightness to the paper. The sulfites used can be calcium sulfite, but in some of the newer mills magnesium sulfite, ammonium, or sodium bisulfites can be employed.

SULFATE SYSTEM OR KRAFT SYSTEM

In the kraft system, the wood chips are boiled under pressure with a solution of sodium sulfide and caustic soda. This solution will dissolve the lignin and other non-cellulose portions. The chemicals are recycled and regenerated.

Sulfide in the kraft process causes a fast dissolving action. Two or three hours are used for digestion. The paper from the kraft process will yield a pulp that is high in yield. The resultant pulp is difficult to bleach to a high degree of brightness. The residue from the chemicals can be reused and the dissolved organic matter is burned for the generation of power and steam. This system can be done either by a batch process or by a continuous process which is more modern and efficient.

SEMI-CHEMICAL PROCESS

In the semi-chemical process some of the same chemical treatment is used as in the kraft process or in the sulfite process, but the treatment is more mild and the final separation is obtained by mechanical means. There may or may not be chemical recovery incorporated into these systems.

WASHING AND SCREENING

The pulp fibers, after having been chemically separated from the lignin and polysaccharides, must be separated mechanically. The coarse fiber must be separated from the fine fiber. Two cleaning operations are used with coarse and fine screening.

There may or may not be a washing or thickening and dewatering between the cleaning operations. All dirt and grit particles are not removed. These are usually removed by a centrifugal cleaner with the fibers held in suspension.

The thickening and dewatering are done to concentrate the pulp to increase its consistency. The water is usually removed by vacuum filters in modern technology. Some washing may be incorporated in the thickening.

BLEACHING

The purpose of bleaching is to produce a brighter pulp. To do this, light absorbing substances such as carbonates and minerals must be removed. The pulp is then bleached by peroxide or hydrosulfide in several stages. A washing cycle is employed after each stage. The water is recycled and reused whenever possible.

The bleached pulp may be dried and made into thick sheets and sent to a paper mill. The mill may be both pulp and paper mill, in which case, the bleached stock or pulp may continue on into the remaining stages of paper manufacture. There are other sources of pulp used by the industry which will include pulp made from jute, flax, cotton, rag and reworked papers. The waste papers may be de-inked by dissolving the ink, then releasing the ink and pigment. This can be removed from the pulp in suspension washing. Reworked papers are used in the manufacture of cardboards and heavy box material. The de-inked and washed pulp is treated and finished much the same as other types of pulp at the mills.

PAPER PRODUCTION

Preparation of the pulp for paper manufacture involves beating and refining, mixing and screening. The function of these operations is to further masticate the fibers, sort them according to sizes in accordance with the type of paper being made to give a degree of smoothness to the finished product. Continued beating opens the fibers, loosening them into the desired lengths, strength, density and optical capacity.

They can then be put into a slurry form and sent through the operations at the paper machine. Additives might now be added, to make the paper more water resistant, opaque, dense or colored and to increase its wet strength.

PAPER MACHINE

The actual forming of the paper is done in a paper machine where the slurry of paper is flowed onto a moving screen. With the vibrations of the screen, fibers are compacted to from a mat as the water is drawn away. The mat is then dehydrated and dried in a cylinder machine. Woolen felts are used to press out the water prior to going through the dryer section which consists of a series of highly polished, steam heated cylinder rolls.

After drying, the surface of the sheet is smoothed with a calender roll and cut to size. Many of the materials used in the manufacture of paper to give it the characteristics which it has, are added in the beaters. These include fillers of organic or inorganic types such as rosins, starches, silicates, clay and others.

The combined wastes from a paper mill, including those from the beater, the paper machine, the bleach equipment, and various other washings are classified broadly as "white water." The chemical composition of this white water will vary considerably depending on the type of paper being made. The total solids will vary from as high as 4,000 or 5,000 mg/l, down to a low of 200 mg/l. It is a slightly alkaline waste. Of the total solids, much of it is caused by suspended fibers. The volume of water in gallons per ton of fiber processed also varies considerably and may go to a high of 25,000 gallons per ton. For a tissue mill, a box board mill, or a heavy cardboard type paper mill, the volume may be as low as 5,000 gallons per ton.

PULP AND PAPER MILL WASTES

Modern paper mills have been designed with stream pollution in mind with effluent treatment considered to be part of the business. The pulp mills that work logs

POLLUTION FROM THE PULP AND PAPER INDUSTRY SOURCES, TYPES, AND METHODS OF ABATEMENT*

Source	Nature of Pollutant	Method of Abatement
Wood Room Debarkers and Screens	Bark, bark fines passing through screens, grit from logs	Bark pressed and burned in bark boiler, ash and grit collected for land disposal fines removed in primary clarifer.
Mechanical Pulping	Fiber fines, grit from stones, BOD (large installations)	Fines removed in primary clarifier, grit settled out in settling chambers, BOD reduced through biological treatment.
Chemical pulping (or cooking) and washing	Fiber fines, soluble organics (BOD), crude soaps, color bodies, soluble inorganics	Fines removed by primary clarifier, clarified effluent treated biologically to reduce BOD by means of aerated lagoons or some modific tion of activated sludge process, crude soaps collected during liquor evaporation and shipped as tall oil or burned concentrations of color bodies and soluble inorganics reduced by dilution in receiving waters.
Screening	Knots, shives, coarse fiber, soluble organics (BOD)	Refined, cleaned, and returned to system; water recirculated; dirt, shives and fines rejected are then removed in primary clarifier, BOD reduced by biological treatment.
Bleaching	Fiber fines, soluble organics (BOD), color bodies, soluble inorganics	Fiber fines removed in pirmary clarifier or settling lagoon, BOD of clarified effluent reduced by biological treatment (lagoons, activated slud process, or modification,. color bodies and soluble inorganics reduced in concentration by dilution.

Source	Nature of Pollutant	Method of Abatement
Paper manufacturing	Fiber fines, clays and other minerals	Filler clays and fiber fines removed in primary clarifier--may require special chemical treatment with alum, lime, or ferric compounds.
Coating (on or off machine)	Coating minerals, binders such as starch have a BOD	Primary clarification, employed to remove coating minerals in suspension, may require special treatment; BOD of clarified effluent reduced in biological treatment.

*From Industrial Pollution Control Handbook, Herbert F. Lund into pulp must necessarily be large operations for the efficient use of the equipment. They process between 200 to 1,000 tons of logs a day. Approximately half of the pollution load from the pulp mill comes from the concentrated solutions in the digesters. These solutions will discharge between 100,000 and 120,000 mg/l total solids and 35,000 to 50,000 mg/l BOD. The remaining suspended solid load comes from the diluted rinse waters.

The total wood pulp production made in 1962 by the kraft sulfate process accounted for 53 percent, the mechanical ground wood 11 percent, soda and semi-chemical process 10 percent, and sulfite system 9 percent.

NATURE OF WASTES

Suspended solids from paper mills consist of particles of bark and silt from the wood room. There are fine fibers and particles from the paper making processes, pulping, coating and filling materials like clay, calcium carbonate, and titanium oxide. Settleable solids comprise 75 to 95 percent of the total solids load. In addition to the settleable organics, there are soluble organic compounds that are removed from the pulp during the pulping operations. These include sugars, carbohydrates, lignosulfonate and other non-fibrous portions of the log. There are also inorganic salts from these chemical processes.

The discharge of large quantities of paper wastes can result in an overgrowth of micro-organisms which will deplete the oxygen from the water making it unsuitable for fish and other forms of aquatic life. Soluble inorganic materials have caused very little trouble so far. An exception is the addition of certain inorganic nutrients, to the water, which aid in the development of algae. Some phosphates that are discharged by the manufacture of pulp and paper may result in the wild growth of algae in the stream.

WASTE DISCHARGE FROM THE SULFITE PROCESS

In the sulfite process, the wood chips are cooked with sulfurous acid and sulfur dioxide and other sulfite salts. The lignin is dissolved along with the other cellulose from the wood and a pulp yield of 40 to 45 percent of the original wood is obtained. An approximate equal weight of soluble lignins and carbohydrates plus one ton of lime and a ton of sulfur are discharged as waste for every ton of pulp produced by this method. The sulfite process was one of the first developed and used in the United States and the chemicals used are cheap. They were discarded rather than recovered by expensive recovery systems. Sulfite pulping is one of the most serious sources of pollution in the pulp and paper industry.

WASTE DISCHARGE FROM THE KRAFT PROCESS

In the case of the bleached and unbleached kraft pulp, the concentrated liquors from the digestion after separation from the fibers are evaporated down to about 50 percent total solids, then further evaporated and finally burned to remove the organic matter. The organic matter and gases serve as fuels and reducing agents for the sodium sulfate. This results in the formation of sodium sulfide and carbon dioxide, in accordance with the equation given below:

The resulting sodium sulfide and sodium carbonate is treated with slacked lime which forms caustic soda and calcium carbonate.

$$Na_2SO_4 + 2C \longrightarrow Na_2S + 2CO_2$$

This sulfide caustic liquor is then recycled for the digestion of more wood into pulp.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3 \downarrow$$

The calcium carbonate can be run through a kiln and will produce calcium oxide which will be used for the recovery of the spent material as previously indicated. Most of the organic matter dissolved during the pulping process is used in the recovery of chemicals.

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$

The pollution load from this process is considerably lower than in the sulfite process.

WASTE DISCHARGE FROM THE SEMI-CHEMICAL PROCESS

In the semi-chemical pulps, the pollution load is midway between the kraft and the sulfite methods in pollution characteristics. Less chemicals are used than in the sulfite method, however, most semi-chemical plants do not have chemical recovery systems for economic reasons.

WHITE WATER WASTES

The effluent from paper making is dependent upon the chemicals used in the particular paper in question. The materials may be enumerated as follows:

(1) the fiber itself
    (a) cellulose (b) lignin (c) wood sugars
(2) dispersed substances extracted during slushing of the stock in the hydropulper or breaker beater
    (a) rosin (b) starch (c) glue (d) casein
    (e) paraffin (f) synthetic resins
(3) dispersed substances added to the fiber and not retained on the paper during its formation (same as 2 above)
(4) coatings added after the paper is formed
    (a) starch (b) casein (c) synthetic resins
    (d) paraffin

WASTELOADS AND WASTEWATER QUANTITIES- OLDER TECHNOLOGY (Wasteload in lbs/ton of Product)

Processes	Suspended Solids	Dissolved Solids	total Solids	BOD	pH	Quantities in gallons/ton
Wood Preparation	40			44	7.2	12,000
Pulping						
Groundwood	30	310	340	16		7,000
Sulfate (Kraft)	27	135	162	52	9.8	20,300
Sulfite	38	2405	2440	362	3.0	14,600
Semichemical	47	108	155	43	6.6	12,000
Screening, Washing, thickening						
Groundwood	14	93	107	47	5.0	10,000
Sulfate	27	231	258	60	9.0	35,000
Sulfite	43	265	308	43	6.3	37,000
Semichemical	47	143	590	120	7.0	28,000

continued

WASTELOADS AND WASTEWATER QUANTITIES- OLDER TECHNOLOGY continued

Processes	Suspended Solids	Dissolved Solids	Total Solids	BOD	pH	Quantities in gallons/ton
Bleaching						
Groundwood	-	-	-	-	-	-
Sulfate	-	-	400	-	-	45,000
Sulfite	30	305	335	40	4.4	43,000
Semichemical	-	-	-	-	-	45,000
PaperMaking	60	100	160	20	-	32,000
TOTAL MILL EFFLUENT						
Bleached Sulfate & Paper	200	900	1100	200	-	110,000
Unbleached Sulfate & Paper	-	-	650	-	-	90,000
Bleached Sulfite & Paper	120	1200	1320	500	-	95,000

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WASTELOADS AND WASTEWATER QUANTITIES OF TODAY'S TYPICAL TECHNOLOGY (Wasteload in lbs/ton of Product)

Processes	Suspended Solids	Dissolved Solids	Total Solids	BOD	pH	Wastewater Quantities in gals/ton
Wood Preparation	9	4	13	3	7.0	3,400
*Pulping:Sulfate	17	141	164	23	11.5	5,600
Sulfite	29	382	411	235	2.5	10,900
Semichemical	22	148	200	30	3.5	7,000
Screening, Washing, Thickening						
Groundwood	11	44	75	33	6.0	7,500
Sulfate	19	185	204	39	9.5	10,500
Sulfite	16	142	158	26	4.0	13,000
Semichemical	3	90	93	24	7.4	55,000

*No Groundwood figures given

WASTELOADS AND WASTEWATER QUANTITIES OF NEWER TECHNOLOGY (Wasteload in lbs/ton of Product)

Processes	Suspended Solids	Dissolved Solids	Total Solids	BOD	pH	Wastewater Quantities in gals/ton
Wood Preparation	2	2	4	0.2	6.9	1,700
Pulping:						
Refining Groundwood	16	34	50	10	6.9	2,000
Sulfate	3.0	78	81	21	10.0	4,600
Sulfite	11	289	305	70	3.0	6,300
Pulp Screening:		Generally no waste produced				
Pulp Washing, thickening, cleaning:						
Refining Groundwood	6	21	27	10	6.2	1,900
Sulfate	15	35	50	8	9.5	2,000
Sulfite	6	62	68	11	3.9	4,100
Bleaching:						
Sulfate	2	123	125	8	4.4	11,500
Sulfite	3	187	90	7	7.0	6,000
Deinking	-	-	-	-	-	-
General Papermaking	30	40	70	10	4.5	7,500

WASTELOADS AND WASTEWATER QUNTITIES OF NEWER TECHNOLOGY, continued

Processes	Suspended Solids	Dissolved Solids	Total Solids	BOD	pH	Wastewater Quantities in gals/ton
Total Mill Effluent (Integrated Pulp and Paper mills)						
Bleached Sulfate and Paper	90	300	390	90		25,000
Unbleached Sulfate and paper	80	180	260	80		16,000
Bleached Sulfite and Paper	50	400	450	100		30,000

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TREATMENT OF PAPER MILL WASTES

The treatment of pulp and paper mill wastes will vary somewhat from one factory to another depending upon the type of paper processed and the type of pulping system used. In all cases, the problem is somewhat similar in that a large volume of solution must be worked.

There is a problem of removal of considerable suspended solids and high BOD. Some of the materials such as the very fine suspended fibers are not biodegradable and contribute to a considerable volume of sludge. The color of the materials are, in general, not biodegradable.

In modern plants where effluent treatment is considered part of the process and solutions are properly recycled, the total pollution load is greatly reduced. In some instances the pollution contribution of certain processes has been entirely eliminated.

The treatment of effluent from the paper mill and paper pulp industries can include four major categories:

1. Pretreatment Facilities - Pretreatment facilities are designed to remove the grit and coarse material and neutralize the alkaline or acid wastes. Much of the alkalinity or acidity of the wastes can be neutralized by properly mixing

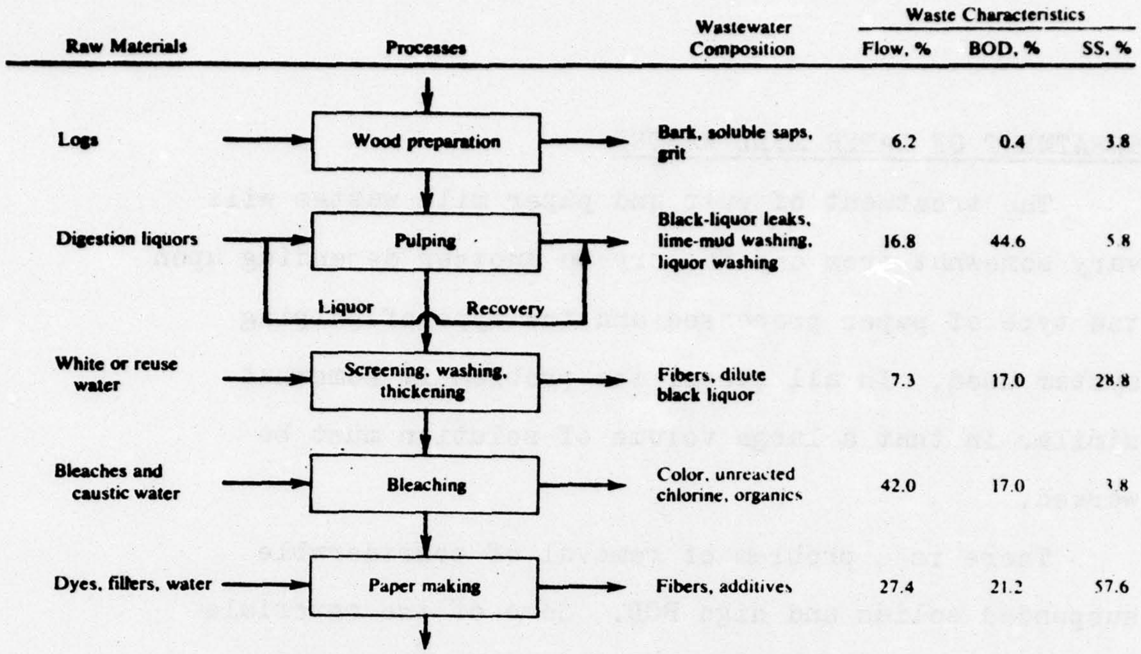

Figure 5.7 Wastewater characteristics from the kraft process.

Table 5.14. Water Reuse and Waste Reduction—Kraft Process[a]

Process	Wastewater	Reuse	Wasteloads Reductions, %	Wastewater Quantities Reductions, %
Wood preparation	Evaporator condensate, bleach pulp washer filtrate	Log flume, debarker, showers	80–90	70–85
Pulping	Recovery condensates	Dilution water, causticizer, screening, de-inking, wood preparation	30 60–90[b]	30 60–90[b]
Screening, washing, and thickening	White water	Makeup water	20–60[c]	20–60[c]
Bleaching			30–80	
Paper machine	White water	Paper machine, stock preparation, bleaching, pulp, washing, and wood preparation	20–70	60–80

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[a] From *The Cost of Clean Water* [*1*].

[b] Liquor recovery.

[c] 60 to 90 percent with multistage countercurrent vacuum filters.

effluents from different sections of the mill. Bleachery wastes can be combined with wash wastes from the pulping operations and this may result in a better sedimentation of the effluent and a reduction in odor.

2. Primary Treatment - Primary treatment is designed to remove the suspended solids and some of the coarse organic matter. The suspended organic matter may be in the form of a colloidal suspension and if this suspension can be broken or coagulated by chemical means, the BOD of the secondary treatment can be greatly decreased.
3. Secondary Treatment - Secondary treatment is designed to remove the BOD and, for this reason, works primarily on the soluble organic portions of the effluent.
4. Tertiary Treatment - The color of the dissolved solids is not easily removed from paper mill effluents by any of the above treatment systems; therefore, certain advance treatments will eventually be required. At the present time the tertiary treatments are a subject of research in the pulp and paper industry, but are not part of the normal commercial treatment practices.

PRETREATMENT SYSTEMS

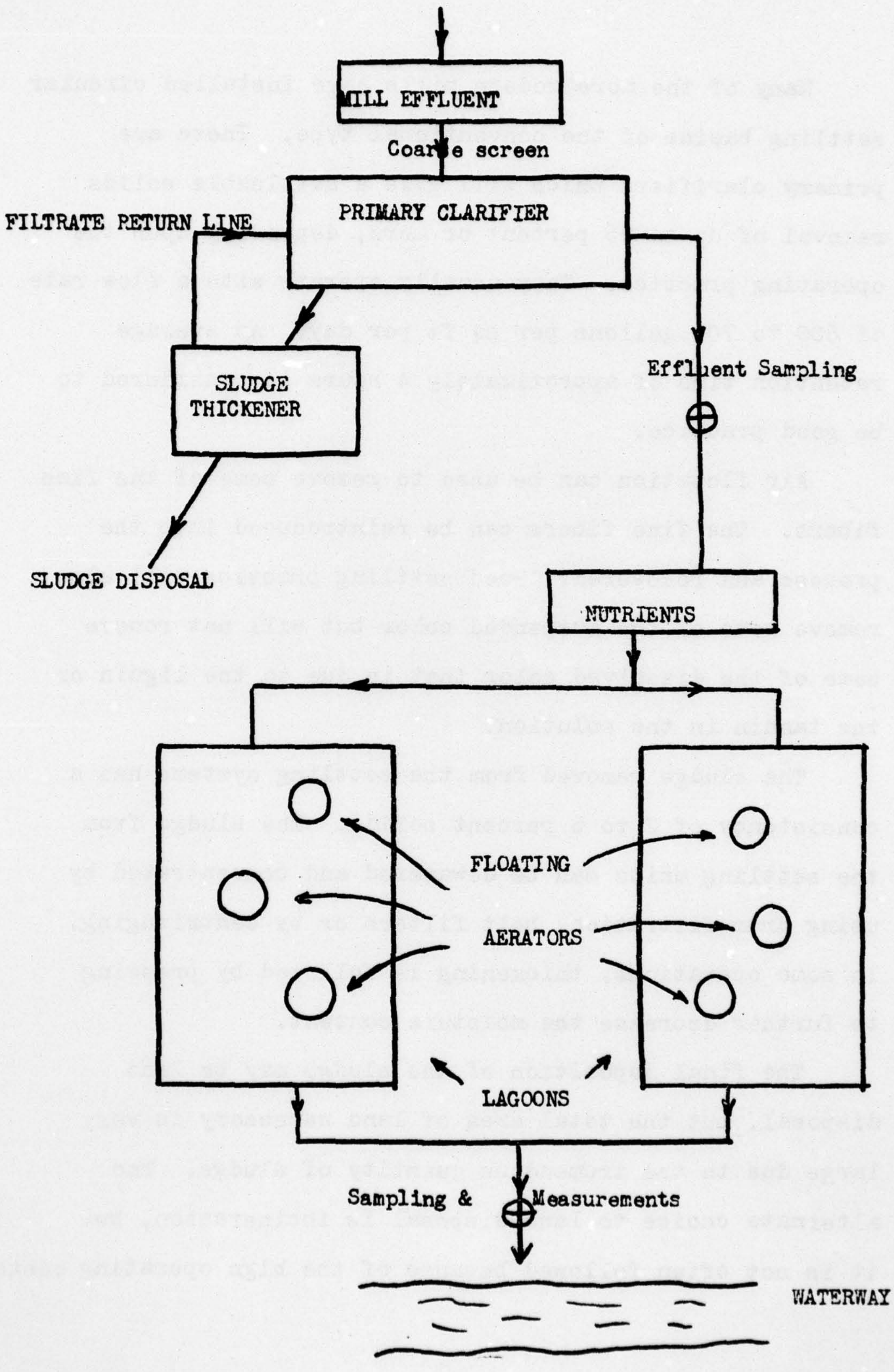
The most common pretreatment system employed is screening to remove the dirt and grit from debarking and some of the washes. The effluent from the screening goes to land fill or burning. The wash water from the pretreatment systems or neutralizing systems go to the primary settling treatments.

PRIMARY TREATMENT

The primary settling is of most importance in paper mill effluent treatment and is in fact the only treatment given in many paper mills. One of the most common systems is a dual parallel lagoon system where sedimentation may take place by alternating from one lagoon to the other, with one lagoon acting as a drying bed while the second lagoon is in use.

The settleable solids may be aided in the flocculation by the addition of alum or iron. This is particularly effective in the removal of rosin and gum. It has been found that shallow lagoons are far more effective than deep lagoons. With the shallow lagoons less than five feet deep, it is much easier to drain the sludge bed. If the sludge bed were very deep, the dewatering of the sludge becomes very difficult.

TYPICAL AERATOR LAGOON SYSTEM



Many of the more modern mills have installed circular settling basins of the conventional type. These are primary clarifiers which will give a settleable solids removal of up to 95 percent or more, depending upon the operating practice. They usually operate with a flow rate of 600 to 700 gallons per sq ft per day. An average retention time of approximately 4 hours is considered to be good practice.

Air flotation can be used to remove some of the fine fibers. The fine fibers can be reintroduced into the process and recovered. Good settling practice will also remove some of the suspended color but will not remove some of the dissolved color that is due to the lignin or the tannin in the solution.

The sludge removed from the settling systems has a consistency of 2 to 6 percent solids. The sludge from the settling units can be dewatered and concentrated by using drum filtration, belt filters or by centrifuging. In some operations, thickening is followed by pressing to further decrease the moisture content.

The final deposition of the sludge may be land disposal, but the total area of land necessary is very large due to the tremendous quantity of sludge. The alternate choice to land disposal is incineration, but it is not often followed because of the high operating costs.

SECONDARY TREATMENT

The waste water from the primary treatment is often sent through equalization facilities in order to correct the pH and even out the temperature. It may be necessary to add nutrients at this point for the secondary treatment. In the case of the mill wastes in which large quantities of alum are used, some of the phosphates added may be taken up in the formation of aluminum phosphate compounds. Under these circumstances additional phosphate will be required.

Under normal conditions one part of phosphorus and five parts of nitrogen are needed per hundred parts of BOD to be removed in a secondary treatment. The choice of biological treatments in a particular installation will depend on the volume of flow and the position of the company relative to capital investment and operating costs. The nature of the waste is also important as is the available land area. The activated sludge process is particularly amenable to the treatment of paper mill wastes and during the past few years, the improved design has resulted in 85 percent BOD removals. This process requires an excellent contact of the oxygen with the solution. This is maintained by forcing air through the system. This will result in the production of about ½ lb of excess biological organisms per lb of BOD removed.

It is necessary to remove these organisms and this is usually done in the secondary clarifier. These clarifiers will have a flow rate of about 800 gallons per day per sq ft. Particularly effective secondary clarifiers have been employed in the industry and effluent concentrations of from 50 - 100 mg/l of suspended solids after this clarification are quite common.

Trickling filters have also been applied. The trickling filters have a tendency to clog with the slimy materials produced. They have a high degree of efficiency to remove BOD at loads of 100 to 700 lbs of BOD per throusand cu ft of media per day. This results in a technically and economically feasible approach in some applications.

Frequently an aerated lagoon is used which will remove from 40 to 75 percent of the BOD present in the mill waste. The large space requirements of this arrangement have been somewhat offset by increasing aeration with floating type equipment. This results in a well aerated lagoon approximately 1 to 2 acres of area per million gallons of waste water flow per day. Roughly 10 lbs of BOD may be applied per thousand cu ft of lagoon volume. Oxidation pounds and stabilized lagoons may also be used. These are of less value in northern climates, but are good in the south where good photosynthetic activity can take place. Lagoons should not be more than 5 ft deep and should receive a loading of about

NORMAL WASTE REMOVAL EFFICIENCIES FOR 1963

Removal Method	Removal Efficiency in % of Gross Waste Load to Each Removal Method			
	Suspended Solids	BOD(5 day)	COD	Color
Primary Treatment:				
Sedimentation Basin	50-90	10-40	10-30	-
Gravity Clarifier	60-90	10-40	10-30	0-10
Dissolved Air Flotation	70-95	20-50	10-40	-
Secondary Treatment:				
Oxidation Pond	0-90	30-50	-	0-10
Trickling Filter	-	30-70	20-50	0-15
Aerated Lagoon	-	40-85	30-60	0-10
Activated Sludge	-	75-95	30-70	10-30
Irrigation	-	60-95	-	-
Sedimentation Basin	60-95	-	-	-
Secondary Clarifier	70-98	-	-	-

These figures are taken from "The Cost of Clean Water", Volume III, U. S. Dept. of Interior

50 lbs of BOD per acre. A typical industry practice provides for 40 to 50 acres of pond area per million gallons of mill waste water.

Irrigation disposal is also possible and is applicable where the land is available so that between 10 and 100 thousand gallons per acre per day can be distributed. Under this system the wastewater should contain less than 200 lbs of BOD per acre per day.

TERTIARY TREATMENT

This treatment is used to obtain a further purification of the wastes, to help remove some of the BOD, color temperature and dissolved solids. Color removal is the usual target for tertiary treatment. Under these circumstances, the investigations have been made on a use of ion exchange or carbon absorption electrodyalisis. Although these systems are expensive, they are effective, and will remove up to 90 percent of the color. There is a limit on the amount of color that can be removed by biological treatment in the waste water from a kraft mill.

One system that works quite well is the massive lime treatment in which the caustic bleaching wastes can be cleaned. Lime is put in for the absorption and chemical reaction on the surface of the lime. The lime is precipitated, dewatered and recausticized.

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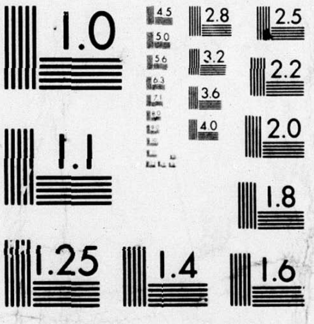

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

There is very little data available on the feasibility of color removal and inorganic solids by treatments like electrodyolisis, reverse osmosis and ion exchange. With the large volumes of water that are needed for the paper industry, the removal of these materials by these advanced treatments does not appear economically feasible.

DISCHARGE INTO MUNICIPAL EFFLUENT PLANTS

One of the main problems of discharging pulp and paper mill wastes into municipal effluent plants is the large volume of effluent from the mill. Most paper mills are located in small towns or rural areas and the effluent would, therefore, dominate the treatment system. The technical difficulties from treating the mill wastes in a domestic system result from the problems of high temperatures, pH, foaming, sulfur compounds, as well as a high suspended solids load and high chlorine demand. We can expect, however, an increase in the joint municipal - industry treatment systems, following a trend of the past. These plants will, probably, be treating wastes that have been given primary treatment at the mill.

WATER REUSE AND BY-PRODUCT RECOVERY

The newer technology in paper manufacture calls for fine screening and recycling of waste water whenever practical. The recycling of chemicals in the kraft process and treatment systems in the new technology greatly decrease the pollution load and volume of effluent. In white water wastes, it has been shown that for some types of paper a complete recycling system can be feasible. Although this cannot be applied in all cases, it does point to a method of completely eliminating the waste from some parts of the industry.

With the more effective waste treatment in the modern technology, there is the possible recovery of valuable wood by-products from spent liquors of the pulping operation. These products include turpentine, tall oil, yeast, alcohols, vanillin, etc.

COST OF EFFLUENT TREATMENT

The capital costs of effluent treatment for paper mills vary considerably with the type of mill, the size, and whether the mill is operating on the new or old technology. The capital costs represent from 2 to 4 percent of the entire capital investment in new mills. The cost of operation may represent from 15 to 30 percent of the original capital cost of effluent treatment per year. Some typical treatment costs are given in the following diagram.

CAPITAL AND OPERATING COSTS FOR "TYPICAL" TREATMENT SYSTEMS

	Bleached Sulfate(Present)			Bleached Sulfite (Present)		
	Small	Med	Large	Small	Med	Large
Total Capital Costs:	714,000	2,314,000	3,140,000	690,000	2,039,000	4,118,000
Capital Cost/Mill capacity in TPD:	7,140	4,630	3,140	1,380	1,360	5,500
Total Annual Operating Cost:	122,700	318,600	574,100	133,200	263,000	962,900
Operating Cost/Mill Production in tons:	3.36	1.74	1.60	7.30	4.80	3.50

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